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Development of the Westvaco Activated Carbon Process for SOx Recovery as Elemental Sulfur. Volume I

Westvaco Corp, North Charleston, S C Charleston Research Center

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

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16. ABSTRACT The report gives results of a demonstration (in a 20,000-cfh integral pilot plant) of an all-dry, fluidized-bed process, using activated carbon for recovering SO2 as elemental sulfur. Granular carbon was recycled continuously more than 20 times between contact with flue gas from an oil-fired boiler and carbon regeneration to recover sulfur. During the 315-hour run, carbon performance remained high with essentially no chemical and low mechanical losses. Over 90% of the 2000 ppm SOx was removed from the flue gas as sulfuric acid by catalytic oxidation and subsequent hydrolysis within the carbon granule. In the two-step regeneration: (1) the acid was converted to elemental sulfur at 300F with internally produced H2S, and (2) an external source of hydrogen at 1000F was used to thermally strip the by-product sulfur from the carbon and produce the required H2S by reaction with the remaining sulfur on carbon. Sufficient process and design information was developed from data obtained in the integral run and prior stepwise pilot equipment operation to permit scale-up to a 15-MW prototype for a coal-fired boiler. In the preliminary design, reducing gas is produced in a coal gasifier. An economic assessment of a 1000-MW conceptual design for the process indicates capital and operating costs competitive with those of other regenerable systems.

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Activated Carbon	Fuel Oil	Elemental Sulfur	11G	21D
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VOLUME I

by

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MANAGEMENT SUMMARY

An all dry fluidized bed SO_2 recovery process using activated carbon has been developed by the Westvaco Corporation to recover sulfur oxides from waste gases with elemental sulfur as a product. The process was developed for five years by Westvaco before joint development with the Environmental Protection Agency (EPA) began in January 1971. During a pause in the contract from December 1971 to September 1972, Westvaco continued development of the process, and then from September 1972 to June 1974 joint development continued with EPA. The process has been shown to be technically feasible and economically attractive compared to other processes currently being developed. Future plans are, therefore, to demonstrate the process at the next stage of development, presently anticipated as the equivalent of a 10 to 20 megawatt coal fired power plant.

In the process the activated carbon catalyzes the oxidation of the sulfur oxides in the flue gas and adsorbs these constituents as sulfuric acid. The carbon is regenerated and the sulfuric acid is reduced to elemental sulfur in unit operations separated from the flue gas clean-up. These two steps of regeneration use a hydrogen containing gas to regenerate the carbon and reduce the sulfuric acid to elemental sulfur by way of an intermediate reductant, hydrogen sulfide, which is produced and recycled within the regeneration system. The regenerated carbon is reused for flue gas clean-up and the elemental sulfur is recovered to be stored or sold.

The demonstration of the activated carbon process for recovering sulfur oxides as sulfur has been completed at an integral pilot plant stage during which a slipstream of flue gas from a 50 MW oil fired boiler was treated. The sulfur oxides were recovered as elemental sulfur of over 99.7% purity for over 300 hours. During the integral run, the activated carbon was continuously regenerated and reused more than 20 times for flue gas clean-up and the carbon maintained its activity with no decrease observed, as indicated by the average removal of 94% of the 2000 ppm sulfur oxides.

The hydrogen requirement of the process was found to be 3.9 moles of hydrogen per mole of sulfur oxide recovered. This hydrogen requirement is 30% above that required by stoichiometry for the reduction of sulfuric acid to elemental sulfur. The recovery process was operated successfully as a closed loop system, as anticipated in commercial operation.

A considerable amount of process development preceded the integral demonstration of the process. The major technical developments were that a granular activated carbon was chosen, the process chemistry established, and the variables affecting the process specified. In addition, the SO_2 removal process step was demonstrated in a multistage fluid bed reactor treating a simulated flue gas and an actual flue gas stream from an oil-fired boiler. A satisfactory design procedure was developed for this process step. The acid conversion to elemental sulfur was also demonstrated in multistage fluid bed equipment and a design procedure was developed. Mechanical constraint, however, necessitated that a moving bed reactor be used in the integral pilot plant run. Several methods of sulfur recovery were assessed, but the stripping of the sulfur with a H_2-containing gas appeared to be most suitable to sustain a high level of SO_2 activity of the regenerated carbon. The sulfur removal and internal H_2S generation steps which finally evolved were demonstrated as a combined operation in one multistage fluid bed reactor. Sufficient information was developed on the carbon regeneration step to, hopefully, insure satisfactory scale-up to the next level of anticipated development.

All of this process and design information which was developed has permitted scale-up to a prototype unit of 15 MW. The preliminary 15 MW demonstration program includes installation on a coal fired boiler and the use of a coal fed gas producer to supply the necessary reducing gas. The installation is anticipated to cost about \$2.4 million to install. The demonstration of the process at the prototype scale is anticipated to require 3 years at a total operating cost of \$1.4 million, or about \$0.5 million/year.

An economic assessment was also made for the recovery process installed at a 1000 MW power plant. The capital investment was estimated to be \$35/KW and the annual operating cost was estimated to be 2.0 mills/KWH. Even though the costs of the process may increase after additional process development information is obtained at the prototype scale, these costs indicate that the process is worthy of consideration for continued process demonstration.

It is concluded that the technical viability and economic competitiveness of the sulfur oxide process developed by Westvaco with partial funding from EPA has been demonstrated.

It is recommended that the process be demonstrated at a prototype stage on a coal fired boiler.

SECTION 1
CONCLUSIONS

The general objectives of the contract were to develop further information on each process step of the Westvaco SO_2 Recovery Process, to demonstrate the technical feasibility of the entire process, to evaluate the performance of the carbon under extended recycling conditions in an integrated pilot plant using flue gas from an oil fired boiler, and to scale up the process to a larger power plant installation.

1.1 CONCLUSIONS - OVERALL PROCESS

1. The process has shown to be technically feasible and economically competitive.
2. The process can use activated carbon to effectively remove flue gas SO_2 and SO_3 and recover elemental sulfur by-product.
3. Sufficient information has been generated on the performance of the activated carbon, process chemistry and pilot operation to proceed to the next stage of development.

1.2 CONCLUSIONS - INTEGRAL PILOT PLANT

The basic conclusions reached in the integral pilot plant are:

1. Granular activated carbon of the type used can effectively remove SO_2 from flue gas and can be regenerated satisfactorily over a repeated number of cycles without reduction in activity or an unacceptable physical loss through chemical reaction or mechanical attrition.
2. Information has been developed on each of the three unit process steps, SO_2 sorption, sulfur generation, and S stripping/H_2S generation, to define the principal variables affecting the process chemistry and their correlations in regard to rate of reaction.
3. An acceptable sulfur product can be produced by the process using hydrogen as a reducing gas with H_2S as an internally generated intermediate reductant.

4. Carbon burn-off is minimized, in fact almost eliminated, in the SO_2 recovery process as proposed.

5. Mechanical attrition of the carbon was acceptable with the improved carbons used in these tests and further reduction by a factor of 3 or more is indicated.

6. Complete reduction of sulfuric acid is not required in the sulfur generator, but part of the acid can be effectively reduced to elemental sulfur in the sulfur stripper/H_2S generator without undesirable side effects, such as an increase in carbon burn-off.

7. The hydrogen requirement of the process was 3.9 moles of H_2 per mole of sulfur oxide recovered for the pilot plant conditions tested.

8. Use of fluidized beds present a viable and attractive method of gas-solids contacting, although other contacting means are also applicable.

9. Operation of the integral pilot plant over the limited time did not appear to present any problems in regard to control of the process.

1.3 CONCLUSIONS - BENCH SCALE

1. The SO_2 removal kinetics are a function of temperature, of gas concentrations of O_2, H_2O, SO_2 and NO and of the acid loading on the carbon.

2. The SO_2 kinetics developed from a bench scale differential reactor could be modeled by an empirical expression and incorporated into a procedure for reactor design.

3. Sulfuric acid adsorbed on the carbon can be converted to elemental sulfur by reaction with H_2S.

4. The kinetics of sulfur generation are functions of acid concentration adsorbed on carbon, of temperature, and of gas concentrations of H_2S and H_2O.

5. The kinetic data of sulfur generation can be represented by an empirical expression and can be incorporated into a procedure for reactor design.

6. Sulfur adsorbed on carbon can be recovered by solvent extraction, but the SO_2 activity of the regenerated carbon can only be maintained at a high level if it is treated further by thermal means.

7. Sulfur adsorbed on carbon can be removed by vaporization and the SO_2 activity is maintained, especially when exposed also to a hydrogen containing gas at the temperature the sulfur is vaporized from the carbon.

8. Equilibrium data of sulfur adsorbed on carbon can be represented by an empirical expression known as the Polanyi-Dubinin adsorption equation.

9. The kinetics of H_2S generation over an activated carbon catalyst can be represented by an empirical expression.

1.4 CONCLUSIONS - PILOT SCALE

1. Multistage fluid bed SO_2 sorber can be effectively used with activated carbon to recover SO_2 and SO_3 from flue gas of an oil fired boiler.

2. Direct flue gas cooling by water spray injection after SO_3 removal can be accomplished in a fluid bed reactor to improve SO_2 removal efficiencies and minimize gas cooling costs.

3. A moving bed reactor for acid conversion to sulfur used in the integral pilot plant because of mechanical limitations associated with a fluid bed reactor was satisfactory for acid conversion.

4. The process steps of sulfur stripping and H_2S generation can be combined into a single operation.

5. Operating temperatures for the existing sulfur stripper/H_2S generator near 1000 to 1200°F are indicated based on sulfur removal from the carbon.

6. A sulfur condenser utilizing recirculating sulfur for a scrubbing fluid is suitable for use in integral operation to recover sulfur from the H_2S recycle gas to the acid converter.

7. A shell and tube cooler is suitable to cool regenerated carbon to be reused in the SO_2 sorber.

1.5 CONCLUSIONS - PROTOTYPE

1. The equivalent of a 15 MW power plant appears to be a suitable size to which to scale up the process.

2. The process information developed to date was sufficient to design an installation of the SO_2 recovery process at a 15 MW power plant.

1.6 CONCLUSIONS - COMMERCIAL (1,000 MW)

1. The SO_2 Recovery Process appears to be economically competitive with other processes now being developed for SO_2 recovery.

SECTION 2
RECOMMENDATIONS

1. Based on conclusions from the integral pilot run and process development to date, it is recommended that scale-up to a larger prototype plant be pursued as the next step toward a commercial plant.

2. The prototype unit should be installed on a coal fired boiler.

3. Provisions should be made to test the prototype installation for use both upstream and downstream of the precipitator.

SECTION 3
INTRODUCTION

The use of activated carbon in dry regenerable SO_2 recovery processes avoids the critical control of chemical reactions necessary in wet processes and the costs and problems involved in separating water from by-product, either for recovery or disposal. Additionally, in the wet processes, flue gas reheating may be necessary for fan protection and plume control. Carbon processes which have or are being used all depend upon the catalytic and sorptive character of the carbon for conversion of the SO_2 to sulfuric acid within the carbon granules. These processes generally differ in the mode of removal and recovery of the sulfuric acid from the carbon. In thermal regeneration, the acid reacts chemically with the carbon to produce a SO_2 rich by-product off-gas. In wet regeneration, the acid loaded carbon is washed with water to produce a weak sulfuric acid. Further differences exist in the additional methods of upgrading the by-product streams through add-on steps for conversion of the SO_2 gas stream to elemental sulfur or concentrated sulfuric acid. The method of contacting flue gas with granular carbon also varies in that fixed beds or moving beds with an upflow or crossflow gas pattern are used. Particle size and characteristics of the carbon granules with respect to the rate of SO_2 removal may differ, affecting pressure requirements and equipment size.

Westvaco, as a major producer of activated carbon, embarked on a program in which carbon, with a high SO_2 pickup rate capability, is recycled with regeneration of the carbon achieved by reducing the sulfuric acid chemically within the process to elemental sulfur and without the carbon being consumed. Furthermore, the fluidized bed was selected for gas-solid contacting as a stagewise approach to permit handling relatively large volume rates of gases in contact with recirculating carbon solids. The effectiveness of fluidized carbon bed systems has been demonstrated in large commercial units in existence, handling gas rates up to 540,000 cfm. The feasibility of using such a carbon system was confirmed in bench scale and small pilot equipment whereby H_2S in contact with the sulfuric acid on the carbon resulted in conversion to elemental sulfur which was then stripped off the carbon by heating and then recovered as a 99.7% pure product. An outside source of hydrogen was reacted with sulfur within the regeneration system to produce the needed H_2S.

The selection of a granular activated carbon and identifying the major variables in the process chemistry served as a basis for the joint work under this EPA contract which essentially involved scaling up the SO_2 removal sorption and the regeneration-sulfur recovery steps to a 20,000 cfh pilot plant. The objectives of the contract were initially to develop further information on each process step and finally to demonstrate the technical feasibility of the entire process and to evaluate the performance of the carbon under extended recycling conditions in an integrated pilot plant using flue gas from an oil fired boiler.

3.1 PROCESS CONCEPT

In the Westvaco Process, dry granular activated carbon is contacted with flue gas at stack gas temperatures. The SO_2 is removed through catalyzed oxidation to SO_3 and subsequent hydrolysis to sulfuric acid which remains sorbed in the carbon granules, i.e.

$$SO_2 + 1/2\ O_2 + H_2O \xrightarrow[\text{Carbon}]{\text{Activated}} H_2SO_4\ \text{(Sorbed)} \qquad (1)$$

Sufficient water vapor and oxygen are present normally in the flue gas for the reaction. This reaction takes place in a staged fluidized bed vessel with provisions for adjusting the temperature for optimum SO_2 removal rates.

The sulfuric acid loaded carbon is transported mechanically to a second fluidized bed reactor wherein the acid comes in contact with hydrogen sulfide to produce elemental sulfur, which remains in the carbon granules, and water vapor which is exhausted. Temperatures near 300°F are required for the reaction, i.e.

$$H_2SO_4 + 3\ H_2S \xrightarrow[\text{Carbon}]{\text{Activated}} 4\ S + 4\ H_2O \qquad (2)$$

Generation of the required hydrogen sulfide and the removal of the elemental sulfur for recovery are accomplished in a third fluidized bed reactor according to:

$$3\ H_2 + 4\ S \xrightarrow[\text{Carbon}]{\text{Activated}} 3\ H_2S + S\ \text{(Product)} \tag{3}$$

The thermal stripping of the sulfur and the reaction to produce H_2S requires temperatures near 1000°F.

$$SO_2 + 1/2\ O_2 + H_2O + 3\ H_2 \xrightarrow[\text{Carbon}]{\text{Activated}} S + 4\ H_2O \tag{4}$$

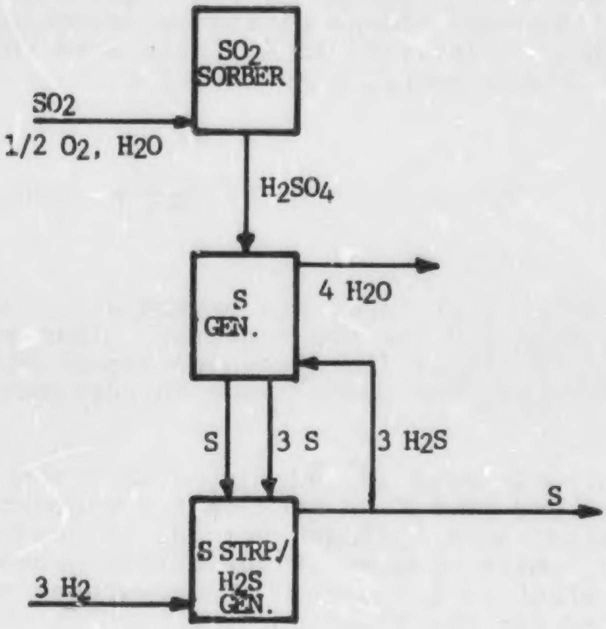

SO2 SORBER
SO2
1/2 O2, H2O
H2SO4
S GEN.
4 H2O
S
3 S
3 H2S
S
S STRP/ H2S GEN.
3 H2

Figure 1. Chemistry of Westvaco SO_2 Process with reactants and products shown

That is, the sulfur dioxide or sulfur trioxide from the flue gas is reduced with hydrogen in the form of recycled H_2S to form water and elemental sulfur.

The hydrogen may be supplied through a number of commercially available gasifiers utilizing coal or other fossil fuels. Heating of the regenerating reactors may be provided by conventional fuel burning units.

The carbon stream, not shown in Figure 1, serves as a carrier and catalyst for promoting the reactions efficiently, but does not directly take part. It is recycled from the SO_2 removal vessel to the regeneration vessels where its activity is restored before returning to the SO_2 sorber.

3.2 METHODOLOGY OF CONTRACT

The main objective of this contract was to achieve integrated operation for a sufficient time to determine the effect on carbon and process performance while treating flue gas from an oil fired boiler. Work was conducted in two parts: from January to December 1971 and from September 1972 to June 1974.

In the first part of the contract, the technical feasibility and design information for the integral pilot plant were to be determined, operating the SO_2 sorber on real flue gas. These objectives were basically completed, with particular emphasis on the flue gas desulfurization step. The kinetics of SO_2 removal were determined with bench scale equipment. The kinetic data were modeled by an empirical expression, which was used in the development of a design procedure for the SO_2 sorber. Concurrent with the bench scale work on SO_2 sorption, a variable study was made with actual flue gas from an oil fired boiler. It was shown that the design procedure developed from bench scale work satisfactorily represented the pilot results. Acid conversion to elemental sulfur was studied extensively in multistage pilot fluid bed equipment. Sulfur recovery from activated carbon was assessed by both thermal and isothermal (solvent extraction) schemes. The evaluation of solvent extraction included testing of a number of solvents. Ammonium sulfide was judged to be the most suitable. The thermal process of sulfur vaporization from the carbon was then compared to the solvent extraction process. The thermal process evolved as the most suitable since the carbon regenerated by extraction required additional thermal treatment to maintain the SO_2 activity, whereas in thermal regeneration, the SO_2 activity was maintained without additional carbon treatment. This process development in the first phase of the contract provided grounds for extended development to be culminated by operation of an integral pilot plant run for an extended period of time.

During the second part of the contract, additional data was to be developed on the regeneration process steps and an integral pilot plant was to be operated. The design information developed was to be used to design and cost a prototype installation for 10 to 15 MW boiler. Also, the cost of a 1,000 MW installation was to be projected. To expedite the completion of these objectives, detailed program plans were drawn up. In the pilot development leading to the integral pilot plant, the two key points were 1) could existing equipment be used for acid conversion to sulfur during integral operation, and 2) could the process steps of sulfur stripping and H_2S generation be carried out in one process unit. It was shown that existing fluid bed equipment could not be used for acid conversion during integral operation. Subsequently a moving bed sulfur generator was designed, installed and operated as part of the preparation for integral operation. It was also shown that the two process steps of sulfur stripping and H_2S generation could be carried out in one reactor. All of the pilot equipment was integrated and operated mechanically on an oil fired boiler, then operated for an extended period to demonstrate long term effects on process and carbon performance.

All performance information was used to design and cost a prototype unit for installation on a 15 MW coal fired boiler. Also the economics of the process for a 1,000 MW installation were assessed.

3.3 CHRONOLOGICAL SEQUENCE OF DEVELOPMENT

Development of the main steps of the Westvaco SO_2 Recovery Process occurred in several phases using various types of equipment. The chronological sequence of development is described for the main steps of the process.

3.3.1 SO_2 Sorption

Pre-contract experimentation with SO_2 sorption was carried out initially in a 1" diameter fixed bed, and later in 4" and 6" diameter multistage fluidized beds. Under the contract, additional work was done in the 6" diameter unit operating on flue gas from an oil fired boiler, and an extensive kinetic study was carried out in a bench scale differential reactor to obtain SO_2 sorption rate data, which were modeled by an empirical expression. An 18" diameter sorber was built and used initially to produce the large quantities of acid loaded carbon needed to study the other steps of the process. The 18" unit eventually was used as the sorber for the integral pilot plant.

3.3.2 Sulfur Generation

Sulfur generation work was begun in a 1" diameter fixed bed reactor but this proved unsatisfactory due to certain inherent disadvantages of fixed beds. Experiments were then carried out in a 4" diameter, 8 stage fluid bed glass reactor and information was obtained on the reaction rate and effects of important variables. A more accurate kinetic study was conducted on a batch differential basis, and this yielded a rate model. After construction of the 4" diameter, 8 stage multipurpose reactor at the powerhouse location, additional sulfur generation tests were made in that reactor to determine whether the 6" diameter reactor could serve as the sulfur generator for the integrated pilot plant. These tests showed that the 6" unit was unsatisfactory for the intended application and efforts were subsequently directed toward development of an alternative moving bed sulfur generator. Bench scale work was conducted in a 1.5" diameter moving bed and the results were used to design an 8" diameter unit, which was installed at the powerhouse location. Sulfur generation studies were made with the 8" diameter moving bed to determine whether its performance was adequate and to optimize operating conditions. Satisfactory performance was obtained from the unit and it became a component of the integrated pilot plant.

3.3.3 Sulfur Recovery and H_2S Generation

In the early stages of the project, two different approaches were considered for the removal of sulfur from carbon solvent extraction and thermal stripping. Solvent extraction was determined to be unsuitable, primarily because the $SO2$ sorption activity of the carbon was reduced excessively by the operation. After abandonment of the solvent extraction approach, efforts were directed toward high temperature thermal stripping. Laboratory data was obtained on the equilibrium adsorption of sulfur on carbon at high temperatures. In addition, a laboratory rate study was made of the H_2S generation steps in a single reactor. The combined operation was studied in the 4" diameter, 8 stage fluidized bed reactor at the powerhouse, and feasibility was demonstrated. The 4" diameter unit functioned as sulfur stripper/H_2S generator in the integral pilot plant runs.

Recovery of sulfur product from the off-gas of the 4" unit required development of a sulfur condensing system. A condenser was designed and fabricated, and tests were conducted. Satisfactory performance eventually was obtained and the sulfur condenser was installed in the integral pilot plant.

3.3.4 Integration

After each of the pilot scale processing units had been operated successfully on an individual basis, they were tied together to form what was termed "the integrated pilot plant". Integration required: 1) closing the carbon flow loop to permit continuous recycling of carbon through the three reactors in the system, and 2) connecting the off-gas line from the 4" diameter sulfur stripper/H_2S generator to the gas inlet of the 8" diameter sulfur generator, permitting operation with internally generated H_2S.

SECTION 4
INTEGRATED PILOT PLANT EQUIPMENT AND RESULTS

4.1 PILOT PLANT DESCRIPTION

4.1.1 Introduction

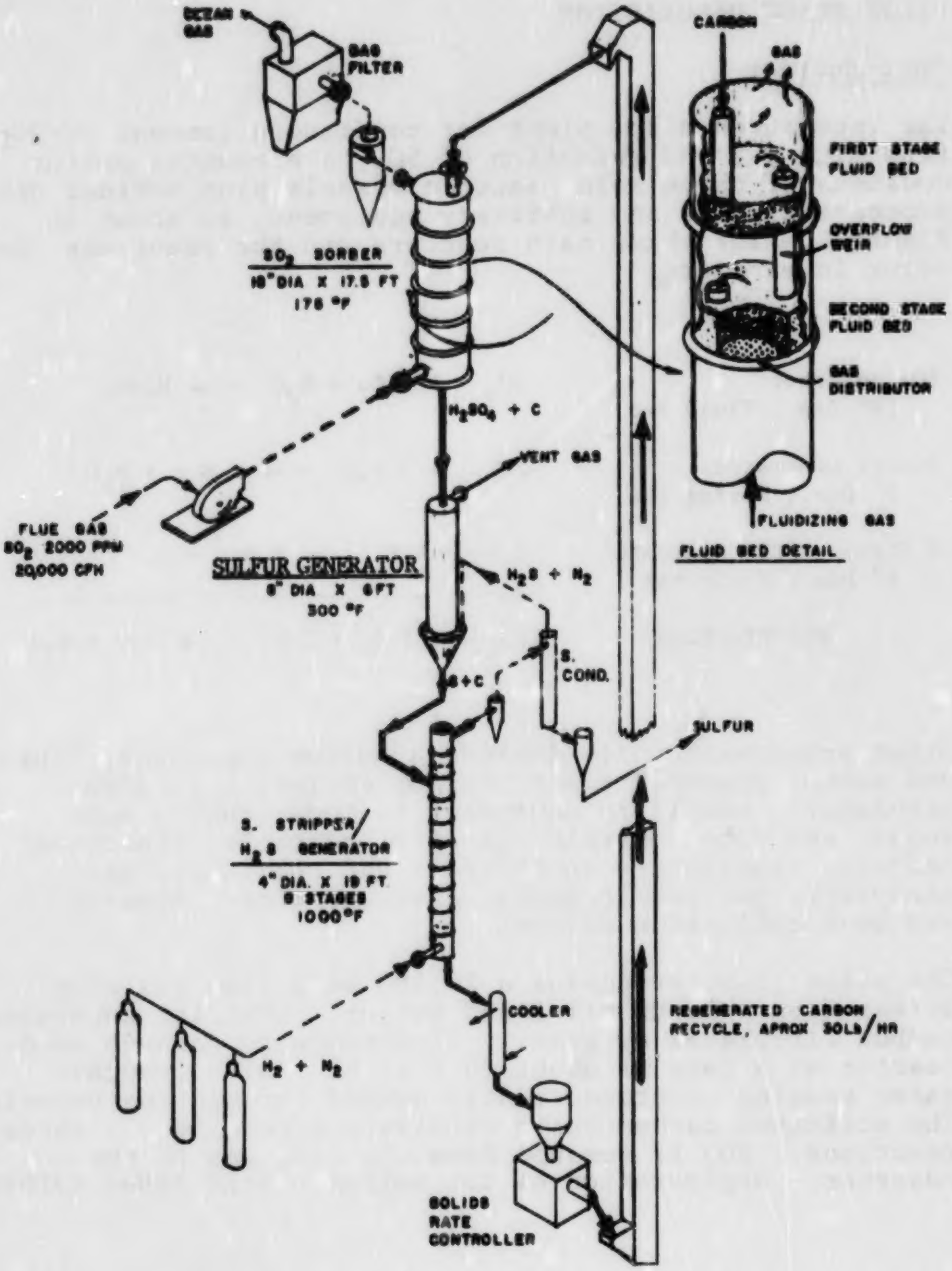
The integrated pilot plant for continuous removal of SO_2 from flue gas and reduction of SO_2 to elemental sulfur consists of three main reaction vessels plus various other processing units and auxiliary equipment, as shown in Figure 2. The three main reactors and the reactions that occur in each are:

SO_2 Adsorber **18" Dia., Fluid Bed**	$SO_2 + 1/2\ O_2 + H_2O \longrightarrow H_2SO_4$	(5)
Sulfur Generator **8" Dia., Moving Bed**	$H_2SO_4 + 3\ H_2S \longrightarrow 4\ S + 4\ H_2O$	(6)
S Stripper/H2S Generator **4" Dia., Fluid Bed**	$3\ H_2 + 4\ S \longrightarrow 3\ H_2S + S$	(7)
NET REACTION	$SO_2 + 1/2\ O_2 + 3\ H_2 \longrightarrow S + 3\ H_2O$	(8)

Other processing units include a sulfur condenser, fluid bed carbon preconditioner, carbon cooler, and carbon preheater. Auxiliary equipment includes carbon conveyors and flow controls, gas flow controls, electrical heaters, temperature controllers and recorders, gas analyzers, gas sample lines, pressure lines, blowers, and dust collection devices.

The pilot plant processes a 20,000 acfh flue gas slipstream from a 50 MW oil fired boiler. Granular activated carbon circulates by gravity flow downward through each reactor at a rate of about 30 lbs./hr., with reactant gases passing countercurrently upward through the vessels. The activated carbon has a catalytic effect in all three reactions. SO_2 is removed from the flue gas in the adsorber. Regeneration of the sulfuric acid laden carbon

Figure 2. Westvaco Process integral pilot plant


CLEAN GAS
GAS FILTER
SO_2 SORBER
10" DIA X 17.5 FT
175 °F
CARBON
GAS
FIRST STAGE FLUID BED
OVERFLOW WEIR
SECOND STAGE FLUID BED
GAS DISTRIBUTOR
FLUIDIZING GAS
FLUID BED DETAIL
H_2SO_4 + C
VENT GAS
FLUE GAS
SO_2 2000 PPM
20,000 CFH
SULFUR GENERATOR
6" DIA X 6FT
300 °F
H_2S + N_2
S. COND.
S+C
SULFUR
S. STRIPPER/
H_2S GENERATOR
4" DIA. X 19 FT
8 STAGES
1000°F
COOLER
REGENERATED CARBON RECYCLE, APROX 30LB/HR
H_2 + N_2
SOLIDS RATE CONTROLLER

is accomplished in the other two reactors. In the sulfur generator the H_2SO_4 is reduced to elemental sulfur by reaction with H_2S. The sulfur remains sorbed on the carbon. In the combined sulfur stripper/H_2S generator, hydrogen gas reacts with about 75% of the sulfur to generate the H_2S for the sulfur generator. The remaining sulfur is stripped from the carbon thermally and leaves the reactor as a vapor in the off-gas. The sulfur vapor is removed from the off-gas in a condenser and recovered in molten form. The sulfur free off-gas containing H_2S then passes to the inlet of the sulfur generator. The regenerated carbon is recycled back to the adsorber. The hydrogen rich gas used to generate H_2S for the sulfur generation step is the only raw material besides activated carbon that is required by the process.

Instrumentation and Control -

Sufficient instrumentation is available to maintain the desired operating conditions during steady state conditions and to collect the data necessary for performance evaluation. All input gas flow rates are monitored through meters and checked by gas analysis instruments. Temperatures and pressures at appropriate points within the system and reactors are either indicated or recorded.

Sample Points and Analysis -

Ports were positioned on the inlet and outlet of each of the three reactors for sampling the granular carbon to determine the amount and form of sulfur and moisture content. Gas sample ports were also positioned so that various inlet and outlet points in the system were analyzed chromatographically for H_2, O_2, H_2S, SO_2, N_2, CO_2, CO and H_2O at the desired time. Samples of the carbon were analyzed using standard tests for measuring the physical and adsorption properties.

Granular Carbon -

The carbon used in the integral pilot operation is a commercially producible coal-based carbon with a nominal 12x40 mesh size and bulk density of about 40 lbs./cu. ft. The SO_2 number and attrition number were 60 minimum and 97 maximum, respectively, as determined by specially designed tests. This carbon showed satisfactory attrition resistance in pilot testing. Carbons with improved resistance are being developed.

Flue Gas Characteristics -

Flue gas used in the integral testing was from the stack of a 50 MW oil fired boiler having a mechanical dust collector. The sulfur content of the oil was about 1.8 - 2.0%, which produces about 1100 ppm SO_2 in the flue gas. In order to avoid variability at this stage of operation, provisions were made for injecting additional SO_2 into the flue gas to maintain a uniform level to the pilot plant. The temperature of the flue gas was kept at stack temperature (300°F) before introducing into the SO_2 sorber.

Reducing Gas Composition -

The reducing gas was a mixture of hydrogen and nitrogen from gas cylinders. Hydrogen content was varied from 40 to 48% of the total flow to establish process requirements.

General Operating Procedure -

In starting up the integral system, a known quantity of carbon, about 500 pounds, was placed in the system and recirculated while preheating with a start-up heater to approach the desired operating temperatures. The switch to flue gas was then made. The temperatures, carbon flow rate, and gas flows and compositions were adjusted to the desired conditions. Manual adjustments were made to the SO_2 added to the flue gas above the actual oil produced SO_2 to maintain a constant level. The amount of carbon placed in the system was sufficient to minimize adding fresh carbon during the integral run and represents about 40% above that needed to fill the reactors and conveying system.

4.1.2 Detailed Pilot Plant Description

A detailed flowsheet of the pilot plant is shown in Drawing 2507 (Figure 3). The following description of the pilot plant equipment is organized to follow the path of the activated carbon as it moves through the system, beginning with the SO_2 sorber. The operation of each processing unit is described also, including important operating conditions and procedures. Equipment identifications are based on the process flowsheet, Figure 3. Instrumentation identifications are based on the instrumentation flowsheet, Drawing 2528A in Appendix B-3.

SO_2 Sorber [RV-10] -

The sorber [RV-10] is an 18" dia. x 17.5 ft. high vessel with five fluidized beds of carbon, each bed having an expanded depth of 12 inches except for the bottom bed which

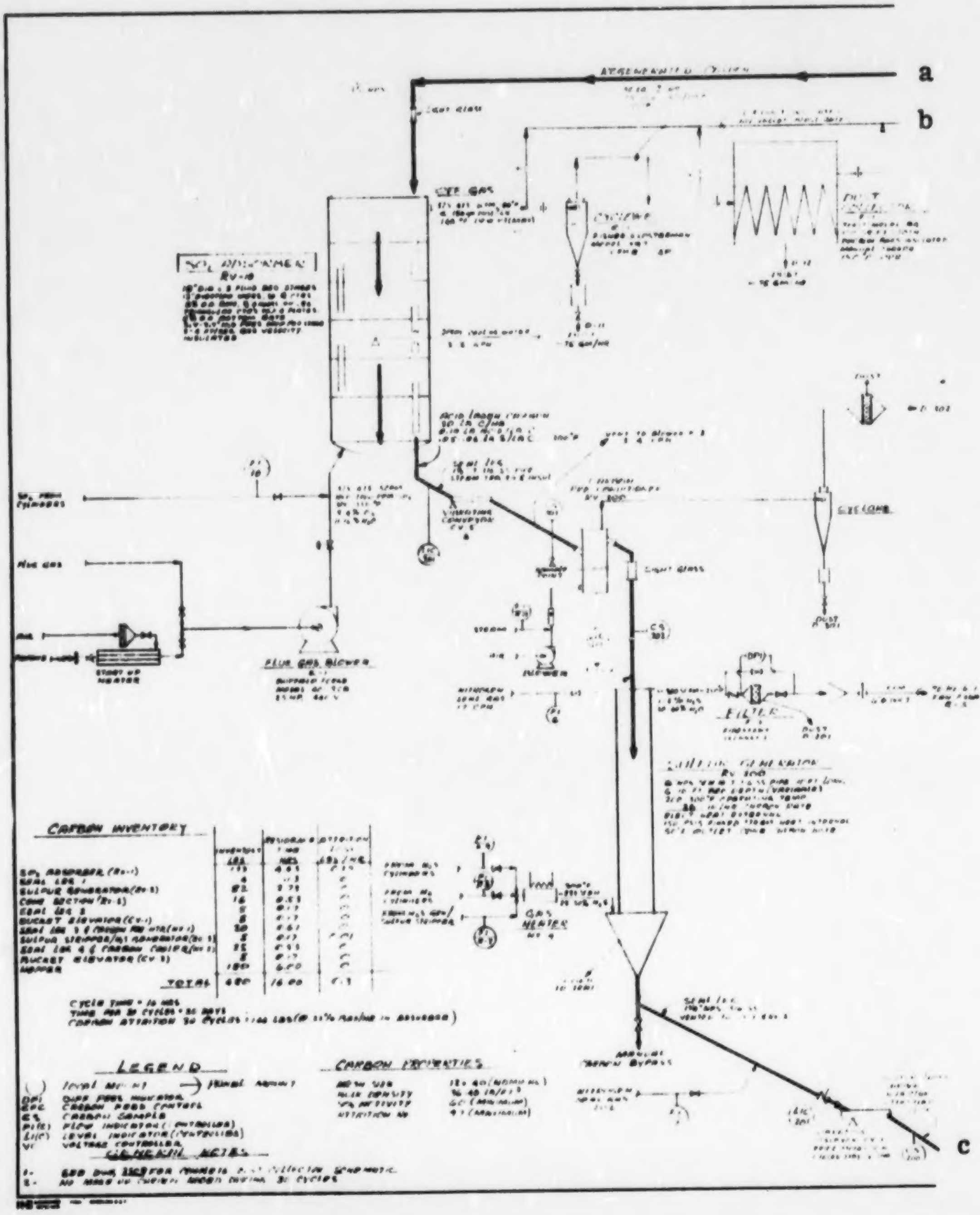

a
b
c
REGENERATED CARBON
FLUE GAS
SO2 ABSORBER
RV-10
CYCLONE
DUST COLLECTOR
SIGHT GLASS
VIBRATING CONVEYOR
FLUE GAS BLOWER
START UP HEATER
SULFUR GENERATOR
RV 300
CYCLONE
FILTER
DUST
GAS HEATER
BLOWER
NITROGEN
CARBON INVENTORY
TOTAL
680
16.00
LEGEND
DPI DIFF. PRES. INDICATOR
CFC CARBON FEED CONTROL
CS CARBON SAMPLE
FI(C) FLOW INDICATOR (CONTROLLER)
LI(C) LEVEL INDICATOR (CONTROLLER)
VC VOLTAGE CONTROLLER
CARBON PROPERTIES
MESH SIZE
BULK DENSITY
ACTIVITY
ATTRITION NO
GENERAL NOTES
MANUAL CARBON BYPASS

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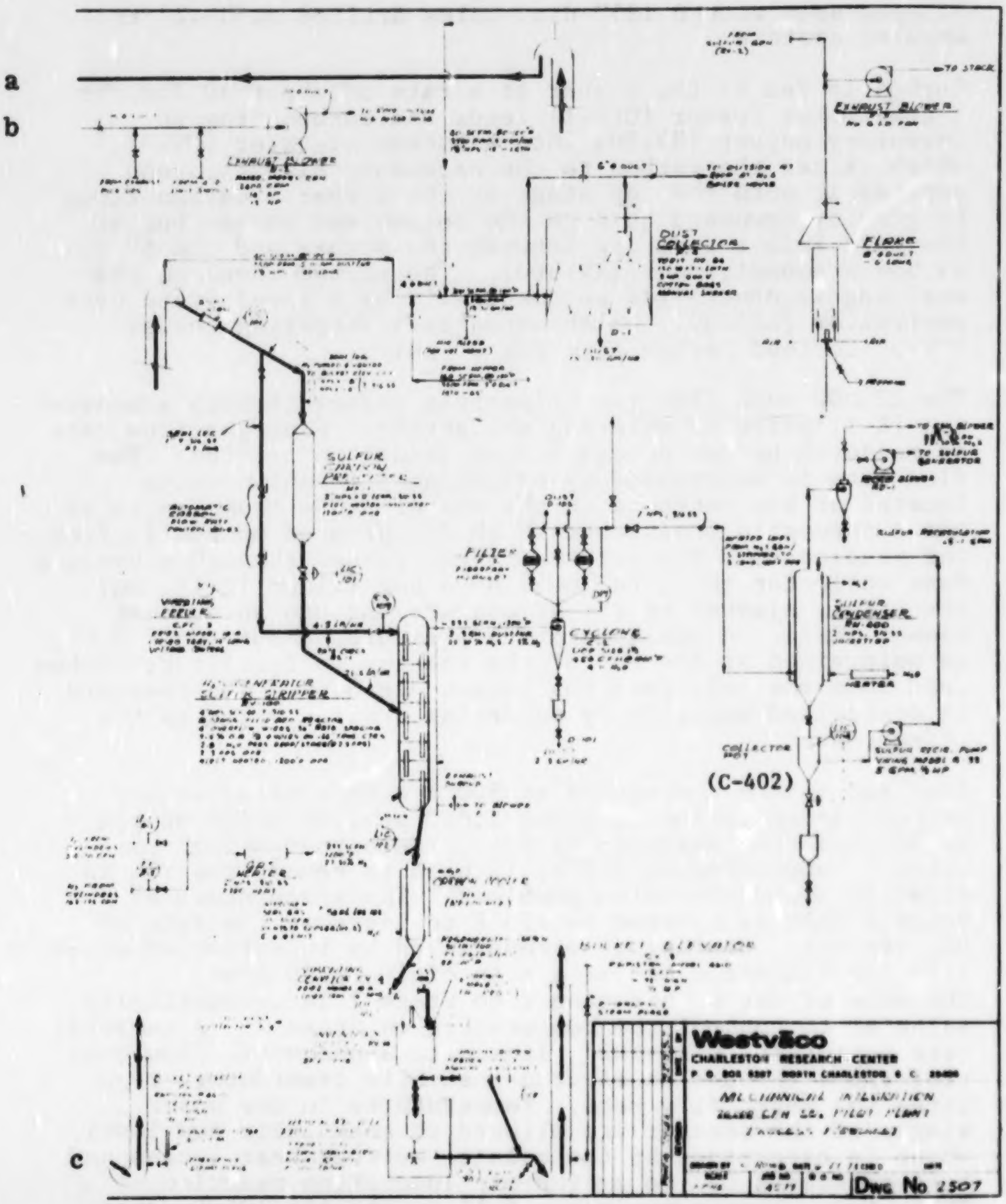
Figure 3. Mechanical integration - 20,000 cfh SO_2 pilot plant - process flowsheet


a
b
c
EXHAUST BLOWER
EXHAUST BLOWER
DUST COLLECTOR
FLAKER
SULFUR CHARGING HOPPER
VIBRATING FEEDER
REGENERATOR SULFUR STRIPPER
FILTER
CYCLONE
SULFUR CONDENSER
HEATER
TO STACK
TO SULFUR GENERATOR
(C-402)
BUCKET ELEVATOR
Westvāco
CHARLESTON RESEARCH CENTER
P. O. BOX 5207 NORTH CHARLESTON S. C. 29406
MECHANICAL INTEGRATION
20,000 CFH SO2 PILOT PLANT
PROCESS FLOWSHEET
DWG No 2507

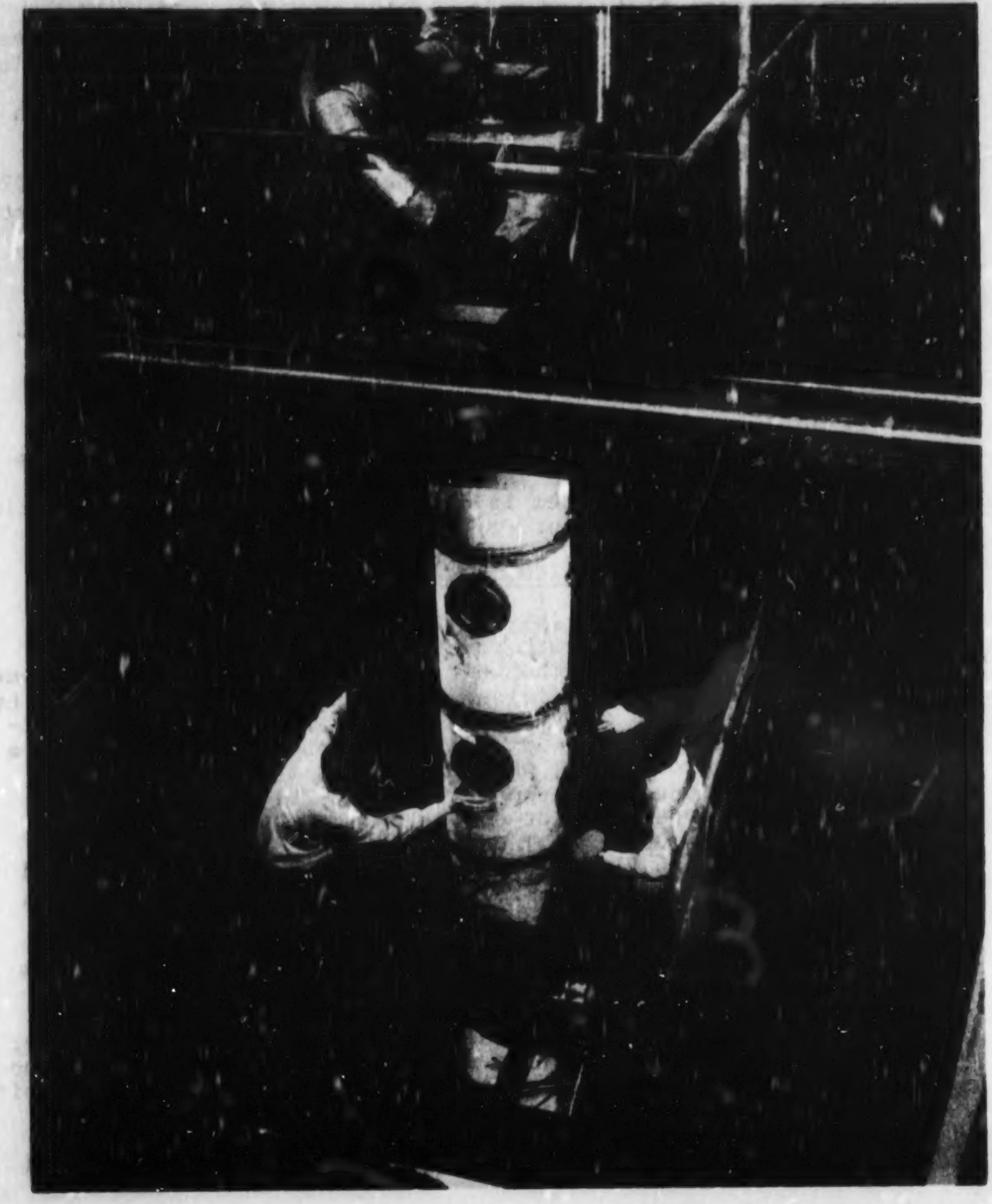
has 8 inches. A photograph of the sorber is shown in Figure 4. Assuming a carbon density of 38 lbs./ft.^{3}, the weight of carbon in the vessel is about 113 lbs. The downcomers are 3" dia. and extend to within 1-1/2 inches of the distributor plates below. The gas distributor plates have 8% open area with 0.125" dia. holes drilled on 0.42" triangular centers.

Carbon is fed to the sorber at a rate of about 30 lbs./hr. A gravimeter feeder [CFC-1] feeds the carbon from an inventory hopper [RV-90] into a bucket elevator [CV-3], which raises the carbon to the necessary elevation and empties it onto the top stage of the sorber. Carbon flows by gravity downward through the column and passes out of the unit into a seal leg between the sorber and the 6" dia. carbon preconditioner [RV-300]. The carbon level in the seal leg is controlled automatically by a level probe type controller [LIC-301] which actuates a vibrating feeder [CV-5] to feed carbon into the 6" unit.

The 22,000 acfh flue gas slipstream passes through a booster fan [E-1] prior to entering the sorber. Flue gas flow rate is measured by the pressure drop across an orifice. The flow rate is controlled by adjusting a trunnion valve located at the entrance to the sorber. The trunnion valve has a pneumatic positioner which is operated mannually from the panelboard. The sorber off-gas passes through a cyclone dust collector [C-1] followed by a bag filter [F-1], and then it is ejected to the atmosphere through an exhaust blower [E-2]. A small negative pressure, about -0.5" W.C., is maintained at the top of the reactor to facilitate carbon feed into the unit from the bucket elevator. The pressure is controlled manually by adjusting a slide valve in the off-gas duct.

Flue gas enters the sorber at 300°F with a total sulfur oxides concentration of about 2,000 ppm, of which 50 ppm is SO_3 and the remainder is SO_2. The bottom bed of the reactor, operating at 300°F, is used to remove the SO_3 in order to avoid corrosion problems. The temperature at Stage 2 then is lowered to 175°F to increase the rate of SO_2 removal. Cooling is accomplished by injection of water into the fluidized bed at a rate of 10 to 50 #/hr.
The rate of water injection into Stage 2 is automatically adjusted to control the temperature on Stage 2. A temperature controller [TIC-102], linked to a pneumatic flow control valve through an electro-pneumatic transducer, regulates the water flow rate. Temperatures in the upper stages of the reactor are allowed to seek their own level, which is determined by the balance between heat losses and heat generated by the exothermic adsorption reaction. These temperatures typically fall in the 180-190°F range.

Figure 4. Continuous 18" dia., 5 stage SO_2 and SO_3 adsorber operating on flue gas from a 50 mw oil fired boiler



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Carbon Conditioner [RV-300] -

The carbon conditioner [RV-300] is a 6" dia. x 2 ft. high single stage fluid bed unit which is used to adjust the temperature and moisture content of the carbon as it passes from the SO_2 sorber into the sulfur generator. The unit is operated at a carbon bed temperature of 320°F, with pure steam or an air-steam mixture as the fluidizing gas. With pure steam, a carbon moisture loading of about 0.10 lb. H_2O/lb. carbon is obtained. The steam flow rate is measured by a rotameter. A temperature controller [TIC-302] controls an electrical heater to maintain the desired inlet gas temperature.

Carbon flow into the 6" dia. conditioner is controlled by the level probe controller [LIC-301] which maintains the proper carbon level in the seal leg between the SO_2 sorber and the conditioner. Carbon passes out of the unit by gravity flow into a seal leg between the conditioner and the 8" dia. moving bed sulfur generator [RV-200]. There is no direct control of the carbon flow out of the conditioner. Instead, the carbon level in the seal leg is maintained by a system which controls the carbon flow out of RV-200. This system is described in the following section on the sulfur generator.

Sulfur Generator [RV-200] -

The sulfur generator [RV-200] is a moving bed reactor, 8" dia. x 10 ft. high, with an actual carbon bed depth of 6 feet. Carbon enters the unit from an upper seal leg between it and the carbon conditioner [RV-300] and flows downward by gravity in essentially a plug flow distribution. A vibrating conveyor [CV-2] feeds the carbon out of the unit into a bucket elevator [CV-1] which transfers it to the next reactor. A pneumatic controller [LIC-201] controls the vibrating feeder so that a constant carbon level is maintained in the upper seal between RV-200 and RV-300. The input signal to LIC-201 is simply the ΔP across the purged seal leg, which is proportional to the height of carbon in the leg.

Reactant gas containing about 30% H_2S enters at the bottom of the vessel and passes upward through the bed, countercurrent to the carbon flow. Total gas flow rate is 185-260 scfh. The source of the reactant gas mixture is either cylinder gases or else the recycled off-gas stream from the 4" dia. S stripper/H_2S generator [RV-100]. When the 4" unit off-gas is used, the pilot plant is said to be operating with "process H_2S". Cylinder gas rates are controlled at the panel board with rotameters. An electrical heater and temperature controller maintain the desired inlet gas temperature of about 300°F when cylinder gases are used. When the pilot plant is operating with process H_2S, the gas is hot already and requires no further heating.

The off-gas from the sulfur generator is exhausted to the boiler house stack on the negative pressure side of an ID fan. A valve in the off-gas line permits adjustment of the pressure inside the sulfur generator at 1 - 5 inches W.C. at the top of the unit to facilitate gas sampling for chromatographic analysis.

The temperature of the carbon bed typically ranges from 260°F at the bottom to 300°F at the top. Ideally the temperature would be near 300°F throughout, but as the reaction approaches completion in the lower section of the bed, less heat is generated by the reaction and the temperature drops off. Temperature is a function of 1) inlet carbon temperature and moisture level, 2) reactant feed rates, and 3) heat input through the walls of the vessel. Three electrical heating mantles, individually controlled with power-stats, are used to regulate heat input through the walls. Heat input by this means is limited by the SO_2 evolution problem at temperatures over 300°F, so that the wall heaters are operated to maintain a wall temperature only slightly over 300°F. Maintenance of proper bed temperature is strongly dependent on the uninterrupted feed of reactants to the unit. Bed temperatures drop rapidly if the feed of either reactant is interrupted.

Sulfur Stripper/H2S Generator -

The sulfur stripper/H2S generator [RV-100] is a 4" dia x 24 ft. high vessel with 8 fluidized beds of carbon, each bed having an expanded depth of 5 inches. Electrical heaters around the unit maintain the temperature at 1000-1200°F. The heaters are controlled automatically by 5 temperature controllers, with one controller for every two stages and the fifth controller for the inlet plenum heater. A sixth controller handles the inlet gas heater.

The unit operates at a linear gas velocity of 2 - 3 ft./sec. with a total gas flow rate of 200-300 cfh at 70°F. Hydrogen and nitrogen are supplied from cylinders and metered through rotameters. Flow rates are set manually. The inlet hydrogen concentration was typically 38-48% (shown incorrectly as 27-30% in Figure 3). The inlet gas is preheated before entering the reactor. The reactor off-gas passes through a cyclone dust separator [C-2] before passing on into the sulfur condenser system, which is described in the next section.

The carbon feed for RV-100 is the sulfur loaded carbon product from RV-200. A bucket elevator [CV-1] raises the carbon above RV-100 so that it can feed by gravity flow into the unit. The carbon flows downward through the reactor and passes into a seal leg connecting RV-100 to the carbon cooler [HX-2]. A level probe controller [LIC-102] maintains the proper carbon level in the purged seal leg by controlling a vibrating conveyor [CV-4] which feeds carbon from HX-2 back into the inventory hopper [RV-90].

There are two carbon feed systems for the sulfur stripper/ H_2S generator. In one, the carbon passes from the bucket elevator into the upper seal leg and then is fed into the reactor through a valve controlled by a pneumatic controller [LIC-101] which maintains a constant carbon level in the seal leg. An 8' section of the seal leg is a carbon preheater [HX-1] with electrical heating and a temperature controller. The other system consists of a pair of ball valves controlled by a set of electronic timers so that the valves open and close alternately, with one valve always closed to maintain a gas seal. This system bypasses the carbon preheater and feeds the carbon directly from the bucket elevator into the reactor. The two feed systems provide a number of options in the operation of the reactor. They can be used simultaneously or separately, and carbon can be fed to various stages in the reactor. During integral operation, the double ball valve arrangement became the primary system and the feed was placed on the fifth stage from the bottom during most of the run.

Sulfur Condensing System [RN-400] -

The sulfur condensing system [RN-400] is shown in detail in Drawing 2537 in Appendix B-3. The sulfur condenser is a combination gas cooler and scrubber in which the hot sulfur-laden off-gas from the H_2S generator/S stripper is quenched from 1000 to 300°F, and the sulfur vapor is removed by scrubbing with liquid sulfur. The condenser is a jacketed baffle tray column, 3" I.D. x 4' long, with overlapping baffles (1/2" overlap) spaced 3/4" apart and occupying a 2' long section of the column. Regenerator off-gas enters below the baffle section and passes upward through the baffles, counter-current to the flow of recirculating liquid sulfur. The gas exits near the top and is passed through a 6" thick wire mesh mist eliminator to remove sulfur mist. The sulfur-free off-gas, containing about 30% H_2S, then goes to the sulfur generator [RV-200].

Liquid sulfur is pumped from the collector pot [C-402] beneath the condenser and introduced above the baffle section. The sulfur flows downward through the baffles by gravity flow and collects in C-402. Recovered sulfur condensed from the gas spills over into a collection pot [C-403] so that a constant inventory is maintained in C-402.

Cooling is provided by water at 250°F passed through the condenser jacket under 40 psig at a flow rate of 1.5 - 2.2 gpm. The cooling water is pumped through a heat exchanger to heat it to the desired temperature.

Pilot Plant Instrumentation -

Pilot plant instrumentation falls into three categories: control, general, and analytical instrumentation. All of the instrumentation is indicated on Figure 3, or on Drawing 2528A in Appendix B-3. Each category of instrumentation is discussed below.

Control Instrumentation -

Instrumentation for control of the pilot plant falls into three main categories which are temperature control, carbon flow control, and gas flow control. Time proportional temperature controllers are used with the wall heaters and gas heaters on the H_2S generator/S stripper and the 6" carbon preconditioner [RV-300], and with the gas heater for the sulfur generator. The wall heaters for the sulfur generator are controlled manually with powerstats. Temperature control instrumentation in the SO_2 sorber consists of a time proportional temperature controller linked to an electro-pneumatic transducer control valve, which in turn regulates the water spray rate.

Carbon flow instrumentation consists of a gravimetric feeder, two sets of electronic level probes which operate vibrating feeders, a set of electronic timers which operate a double ball valve feeder, and two pneumatic controllers. One of these operates a carbon flow metering valve, and the other controls a vibrating feeder, through an improvised mechanical linkage of pneumatic and electrical signals.

Gas flow rates are set manually by means of rotameters and metering valves, except in the SO_2 sorber where an orifice is used to measure the flow rate, and a piston-actuated trunnion valve equipped with a positioner is used to control the flow rate by means of a manual loading station.

The rate of liquid sulfur recirculation in the sulfur condenser system is controlled by manual adjustment of a variable speed SCR drive on the positive displacement sulfur pump. Temperature in the condenser is controlled by varying either the cooling water flow rate or its temperature. Flow rate is set manually with a valve, and temperature is controlled by adjustment of the steam pressure on the heat exchanger used to heat the water to the desired inlet temperature.

General Instrumentation -

The primary functions of non-control type instrumentation are to provide temperature, pressure, and flow rate data. Three instruments are used for the temperature data, including an Acromag 10 point digital indicator, a Honeywell 24-point strip chart recorder, and a Doric 40-point data logger. The temperatures considered most indicative of pilot plant operation and most important to follow appear on the Acromag digital indicator. The same ten temperatures and a few others appear on the Honeywell strip-chart recorder, which provides a graph showing variation with time. The same ten and thirty more, representing all of the important process temperatures, are recorded by the Doric data logger in numerical form, either automatically at 30 or 60 minute intervals or else manually whenever a printed record is desired. The indicated, logged and recorded temperatures are depicted by TI, TL and TR, respectively, on Drawing 2528A in Appendix B-3.

Pressure measurements are useful in diagnosing the operating condition of the pilot plant. Differential pressure gauges were used to measure pressure drop across each unit and also across each stage within the fluid bed units. This provided information on whether or not carbon flow is satisfactory and reveals any buildup in the system. Pressure drop across an orifice is used to measure gas flow rates at four places in the system.

Analytical Instrumentation -

Analytical instrumentation provides gas composition data for the inlet and outlet gas streams of the SO_2 sorber and regenerator units. The SO_2 sorber gas streams are analyzed for SO_2 concentration using an EnviroMetrics, Inc., Series NS-200 SO_2 analyzer from which output is recorded on a strip chart recorder. Gas streams in the regenerator units are analyzed by a Bendix process chromatograph for seven components: H_2S, H_2O, SO_2, CO, H_2, CO_2 and N_2. The chromatograph can analyze five samples per hour. Peak heights for each component are read from recorder, modified for bar chart display.

Carbon Dust Collection -

Carbon dust is removed from the off-gases of the H_2S generator/sulfur stripper and the SO_2 sorber. Equipment also was installed for dust removal from the 6" carbon preconditioner off-gas, but it was necessary to bypass this equipment due to operational difficulties. The SO_2 sorber is responsible for the major portion of the carbon dust generated in the process. The sorber off-gas first passes through a cyclone and then through a bag filter to remove the finer particles. The combined dust removal efficiency is greater than 99% by weight.

Dust is removed from the off-gas of the H_2S generator/sulfur stripper by a cyclone followed by a specially designed filter containing a 4" depth of Fiberfrax Long Staple Fine ceramic fiber material. The Fiberfrax filter was bypassed, however, after it was found that the small amount of carbon dust did not create problems in sulfur condenser operation.

Sulfur Collection -

Sulfur condensed from the regenerator off-gas is recovered as a liquid by draining the collection pot into a 6-liter metal beaker at 8-hour intervals or more frequently if desired. The sulfur is then weighed and transferred to a larger container for storage.

The recovered sulfur is analyzed for purity either by a combustion analysis in which the carbon impurity is measured as CO_2, or by a sulfur vaporization analysis in which the impurity is measured after vaporizing away the sulfur. Ash content is also determined by a standard ash analysis.

4.2 INTEGRAL PILOT PLANT RESULTS

The broad goals of the Westvaco Process are as follows:

1) High SO_2 removal
2) Minimum hydrogen use
3) Maximum SO_2 recovery as elemental sulfur
4) Minimum carbon burn-off.

With respect to these broad goals for process operation, an original set of goals were defined based on studies of each of the process steps separately. Another set of goal bases which are directed to these broad goals and the main process streams shown in Figure 5 are:

1) SO_2 Sorber
    a. SO_2 removal

2) Sulfur Generator
    a. Sulfur compounds evolved/SO_2 removed

3) H_2S Generator/S Stripper
    a. H_2 utilized/SO_2 removed
    b. Carbon burn-off/SO_2 removed

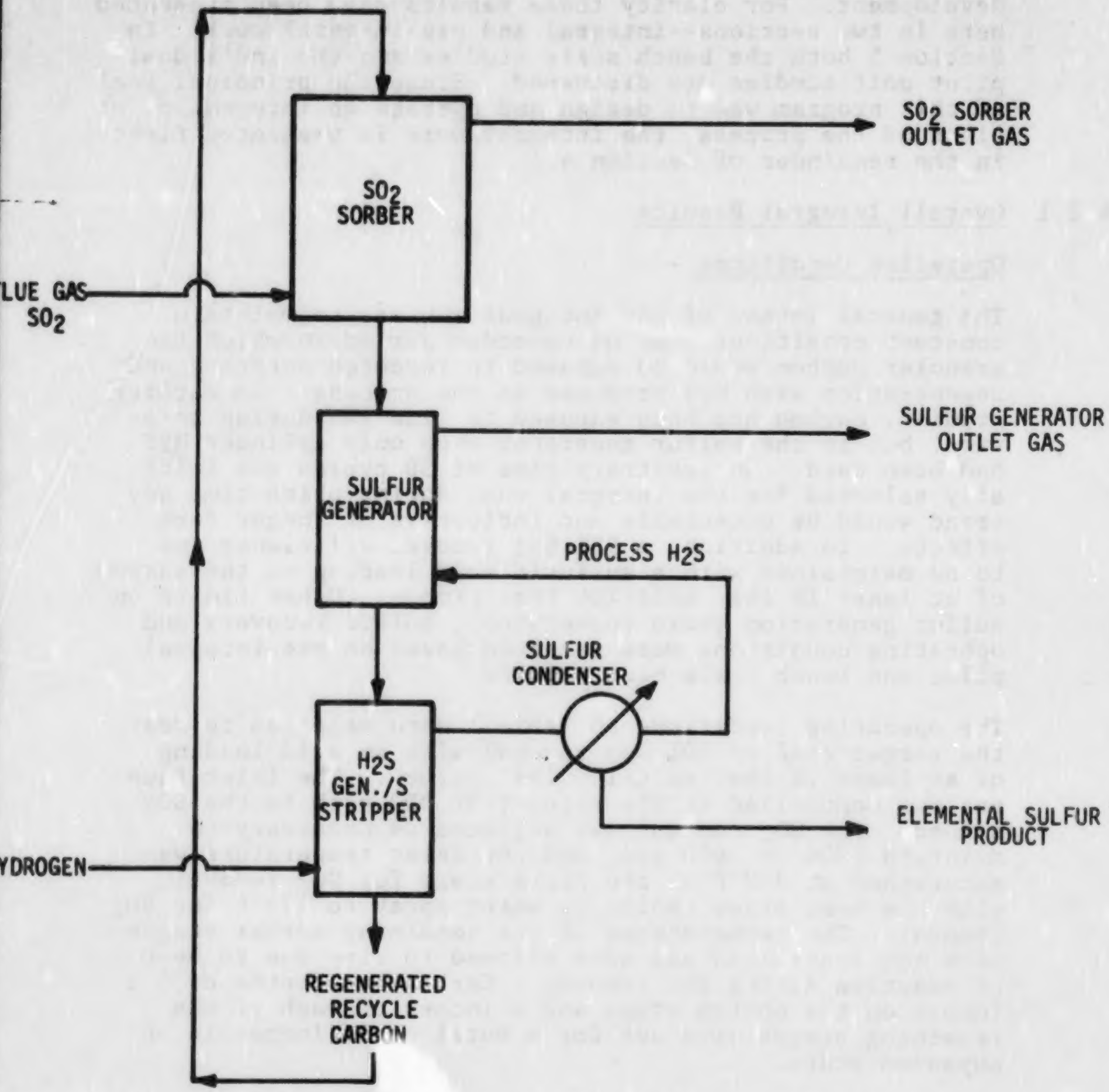
4) Sulfur Condenser
    a. Sulfur recovery/SO_2 sorbed.

The basic difference compared to the original set of goals is that in the latter case only streams that cross the integral process boundary are chosen and in the former case some of the goals were based on internal recycle streams.

The integral run, which totalled approximately 20 days, was made with pilot equipment installed at an oil fired boiler. A mechanical problem, which is described in Appendix B-2, was developed after 11 days or about 18 carbon cycles; it was corrected and did not reoccur during subsequent integral operation. The second part of the integral run was voluntarily stopped after an additional 8 days or about 11 carbon cycles.

To allow continued evaluation of the carbon performance for additional carbon cycles, the same carbon was used in the entire run. In total, the carbon was circulated integrally for approximately 29 cycles to allow evaluation of carbon attrition for this particular carbon. Of these 29 cycles, the carbon was exposed to flue gas/regeneration gas conditions for 21 cycles of which 14 were with process H_2S. Since the source of the H_2S, i.e. process or cylinder, had no apparent effect on SO_2 sorption, 21 cycles were taken as the process exposure time in analyzing the SO_2 removal performance of the carbon.

Figure 5. Schematic of integral Westvaco SO_2 removal pilot plant


SO2 SORBER
OUTLET GAS
SO2
SORBER
LUE GAS
SO2
SULFUR GENERATOR
OUTLET GAS
SULFUR
GENERATOR
PROCESS H2S
SULFUR
CONDENSER
H2S
GEN./S
STRIPPER
ELEMENTAL SULFUR
PRODUCT
YDROGEN
REGENERATED
RECYCLE
CARBON

The development of the Westvaco SO_2 Recovery Process encompassed bench scale studies, pre-integral pilot scale testing, and integral pilot plant operation. Many experiments were performed in each of the phases of process development. For clarity these results have been presented here in two sections--integral and pre-integral work. In Section 5 both the bench scale studies and the individual pilot unit studies are discussed. Since the principal goal of this program was to design and operate an integral pilot plant of the process, the integral work is presented first in the remainder of Section 4.

4.2.1 Overall Integral Results

Operating Conditions -

The general intent of the integral run was to maintain constant conditions over an extended period in which the granular carbon would be exposed to repeated sorption and regeneration with H_2S produced in the process. In earlier studies, carbon had been exposed to flue gas during sorption, but in the sulfur generator step only cylinder H_2S had been used. An arbitrary time of 30 cycles was initially selected for the integral run, during which time any trend would be detectable and indicative of longer term effects. In addition, a 90% SO_2 removal efficiency was to be maintained with a sulfuric acid loading on the carbon of at least 18 lbs. acid/100 lbs. carbon. Other limits on sulfur generation (acid conversion), sulfur recovery and operating conditions were selected based on pre-integral pilot and bench scale test results.

The operating conditions in Table 1 were selected to meet the target goal of 90% SO_2 removal with an acid loading of at least 18 lbs. acid/100 lbs. carbon. The inlet flue gas was controlled at the rate of 22,000 scfh to the SO_2 sorber. The SO_2 content was adjusted as necessary to maintain 1900 to 2000 ppm, and the inlet temperature was maintained at 300°F on the first stage for SO_3 removal, with the next stage cooled by water spray to 175°F for SO_2 removal. The temperatures of the remaining sorber stages were not controlled and were allowed to rise due to heat of reaction during SO_2 removal. Carbon bed depths of 3.5 inches on the bottom stage and 6 inches on each of the remaining stages were set for a total of 56 inches in an expanded state.

The recycle rate of carbon was set to achieve the desired acid loading based on the previous relationships developed between the operating parameters in the sorber.

Table 1. RANGE OF OPERATING CONDITIONS FOR INTEGRAL PILOT PLANT RUN

	CONDITION
INLET FLUE GAS	
Gas Rate:	22,000 SCFH
Temperature:	300°F
Composition, SO_2:	1900-2000 PPM
SO_3:	50 PPM
NO:	150 PPM
O_2:	4.5 Vol. %
H_2O:	13 Vol. %
Inert Gas (CO_2, N_2):	Balance
SO_2 SORBER	
Temperature, Stage 1 (Bottom):	300°F
Stage 2 (H_2O Spray):	175°F
Carbon Bed Depth (Expanded):	Stage 1 - 8" Stages 2 to 5 - 12"
Fluidizing Velocity:	3.5 Ft./Sec. @ 300°F
Space Velocity:	3400 SCF Gas/CF Carbon-Hr.
REGENERATORS	
Acid Converter	
Temperature:	290°F (Avg.)
H_2S Inlet Rate:	Output from H_2S Gen. Range = 2.5-2.9 mol/moles
Space Velocity:	100 SCF Gas/CF Carbon-Hr.
S Stripper/H_2S Generator	
Temperature:	1000-1100°F
H_2 Inlet Rate:	3.4, 3.9, 4.3 moles H_2/mole SO_2 Sorbed
Space Velocity, Stripper:	2000-3100 SCF Gas/CF Carbon-Hr.
H_2S Generator:	6200-9300 SCF Gas/CF Carbon-Hr.
Fluidizing Gas Velocity:	1.8 - 2.7 Ft./Sec. @ 1000°F
CARBON RECYCLE RATE:	29 - 30 Lbs. C/Hr.

Temperature and space velocity conditions for the sulfur generator and sulfur stripper/H_2S generator were based on earlier process unit test results. The hydrogen flow to the generator was varied above the stoichiometric requirement of 3 moles/mole of SO_2 sorbed on the carbon. The amount of H_2S entering the sulfur generator was predetermined by the hydrogen input, with no further attempt to control this rate.

The pilot plant was started and operated for 315 hours under these conditions using previously described procedures.

Summary of Results -

The overall results of the integral run were as follows:

No. of Process Cycles:	21
No. of Operating Hours:	315
Outlet SO_2:	120 ppm
Avg. SO_2 Removal:	94%
Product Sulfur:	99.7% Pure
Carbon Attrition:	0.26 lb./hr.

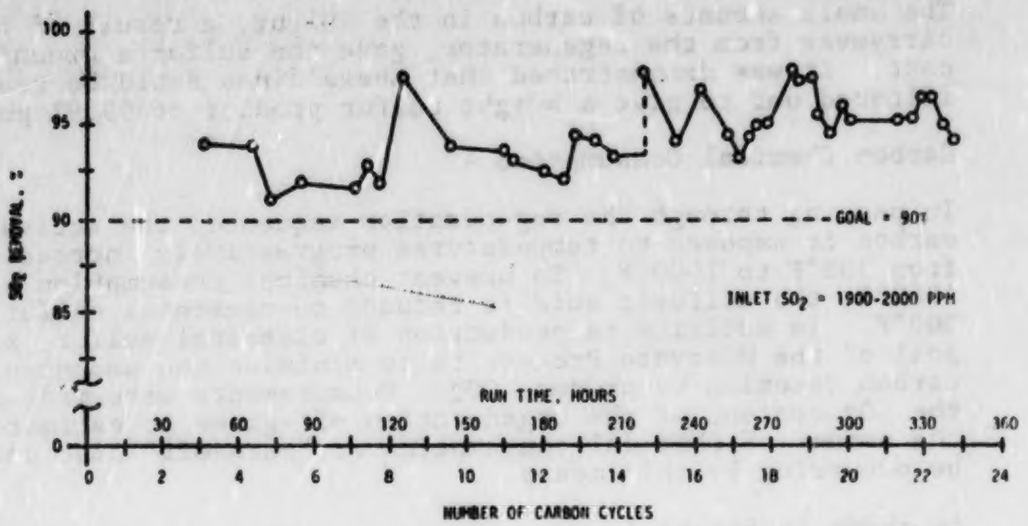
Discussion of Major Response Parameters -

The main factors observed in the pilot operation were the degree of SO_2 removal during cycling of the carbon, the requirements for hydrogen for H_2S generation, and the conversion of SO_2 to elemental sulfur. Other factors were the loss of carbon by chemical and/or mechanical means and the disposition of any excess hydrogen.

SO_2 Removal Efficiencies -

The removal of SO_2 during the 300 hour period of the integral run is given in Figure 6. The flue gas, containing 1900 to 2000 ppm SO_2, was desulfurized to well above 90% with a maximum of 97%, corresponding to 60 ppm remaining in the effluent gas. By inspection of the plot, there does not appear to be any trend toward reduction in SO_2 removal efficiency. This has also been substantiated by laboratory analysis of the recycled carbon. During the integral run, the carbon was cycled through the system some 21 times, based on a calculated carbon residence time of 15 hours in the integral system. The amount of SO_2 picked up by the carbon in terms of sulfuric acid averaged 24 lbs./100 lbs. carbon, substantially above target.

Figure 6. SO_2 removal efficiency during integral pilot tests



No corrosion or dew point problems were noted in operation at 175°F, since the 30 - 50 ppm gaseous SO_3 in the flue gas is adsorbed on the carbon. This removal of SO_3 with carbon was demonstrated in previous studies.

The 150 ppm NO in the flue gas is not directly affected by the carbon and as such remains in the flue gas. The initial effect of the NO is to suppress the SO_2 pickup. This effect appears up to a NO concentration of about 150 ppm. This aspect is covered more fully in Section 5.21.

Sulfur Product -

It is important that the sulfur by-product from the regeneration system be a salable commodity. The elemental sulfur recovered from the pilot tests had characteristics as shown in Table 2.

Table 2. PROPERTIES OF SULFUR PRODUCT

Sulfur	99.7%
Ash	380 ppm
Carbon	2500 ppm
Acidity	2 ppm
Chloride	<2 ppm

These properties, measured for Westvaco by a sulfur producer, classify the sulfur collected as a commercial grade.

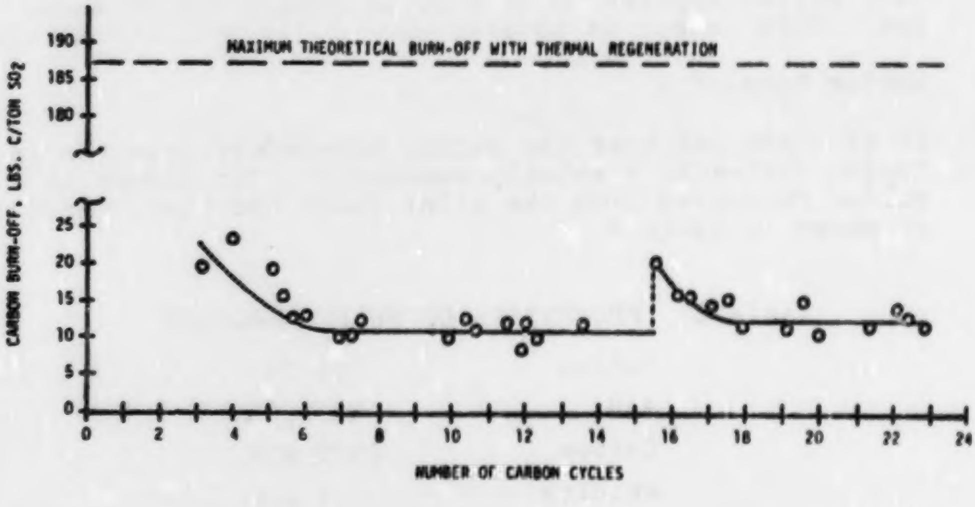
The small amounts of carbon in the sulfur, a result of fines carryover from the regenerator, gave the sulfur a greenish cast. It was demonstrated that these fines could be readily filtered out to give a bright sulfur product of 99.9% purity.

Carbon Chemical Consumption -

In passing through the regeneration sequence, the activated carbon is exposed to temperatures progressively increasing from 300°F to 1000°F. To prevent chemical consumption at 1000°F, the sulfuric acid is reduced to elemental sulfur at 300°F. In addition to production of elemental sulfur, a goal of the Westvaco Process is to minimize the amount of carbon reaction to produce CO_2. Measurements were made on the CO_2 content of the regeneration off-gases to estimate the amount of chemical consumption or "burn-off" that could be occurring by this means.

As shown in Figure 7, the carbon burn-off, calculated from CO_2 evolution reached a stable value of about 10 - 12 lbs. C/ton of SO_2 sorbed from the flue gas. As shown by the dotted line this compares to a "burn-off" of 187 lbs./ton if the carbon were consumed by reacting with all the sorbed acid under thermal regeneration conditions. This

Figure 7. Carbon burn-off during integral pilot tests



reduction in burn-off of about 95% shows that the original objectives were achieved. By inspection of the data there was no apparent effect on burn-off when the hydrogen input was varied in the range of 3.9 - 4.6 moles/mole acid discussed earlier.

Complete conversion of the acid to sulfur was not required to prevent burn-off. Earlier experiments on the bench scale verified this fact, in that the addition of sulfur by various means considerably reduced the chemical consumption of the activated carbon during regeneration.

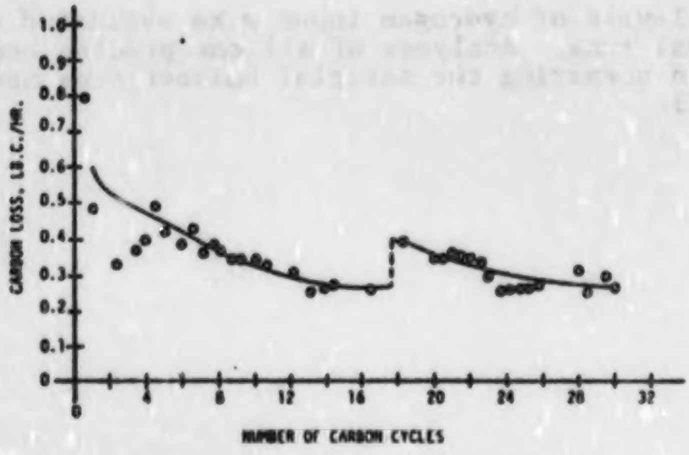
As discussed earlier there was some thermal decomposition in the sulfur generator which would probably explain the small amount of burn-off measured.

If all of the CO_2 measured is a result of burn-off, the low values measured here would correspond to a complete replacement of the inventory only about once every two years.

Carbon Mechanical Consumption -

The attrition rate experienced in the integral pilot operation, Figure 8, showed an initial decrease, probably due to a rounding off of rough edges, and then a stabilization at a rate of 0.26 lbs./hr.

Figure 8. Activated carbon attrition rate during integral pilot tests



The data indicated nearly all of this attrition occurred in the fluidized beds of the SO_2 sorber. Additional work has shown that the combination of larger particle sizes and carbons with improved hardness will reduce the attrition rates to about 10% of the values measured here. These improvements should be incorporated in future scale-up work.

It is significant that there is no apparent increase in the attrition rate as the carbon was recycled thermally and chemically, as has been observed with other solid adsorbents. The nature of SO_2 recovery with carbon, providing a surface for catalysis and adsorption rather than actually chemically participating in the reactions as is done with metal oxides, probably results in the maintenance of structural integrity and strength of the carbon.

Regeneration Results -

In the integral runs, the intent was to demonstrate that the carbon could be repeatedly regenerated for reuse and to maximize the amount of elemental sulfur produced within the limitations of the present pilot equipment. The only deliberate change in regeneration conditions was in the hydrogen input. Other conditions were pre-set based on prior work.

As discussed in the preceding section, the activated carbon retained its adsorptive capabilities throughout the run, attesting to the suitability of regeneration under all hydrogen input conditions.

Three levels of hydrogen input were evaluated during the integral runs. Analyses of all the process streams were used in preparing the material balance presented in Table 3.

Table 3. EFFECT OF HYDROGEN INPUT ON BY-PRODUCT RECOVERY

	Condition A	Condition B	Condition C
TOTAL HYDROGEN INPUT (moles/mole available acid)	4.6	4.3	3.9
HYDROGEN USAGE (moles/mole available acid)			
1. Formation of by-product sulfur	2.90	2.88	3.0
2. Reaction with by-product sulfur to form H_2S	0.25	0.11	0
3. Reaction with chemisorbed oxygen to form H_2O	0.90	1.0	0.9
TOTAL MEASURED H_2 OUTPUT	4.05	3.99	3.90

Condition C essentially represents the process hydrogen input necessary for conversion of the available acid to elemental sulfur product. The hydrogen input above the stoichiometric ratio of 3 reacted with chemisorbed oxygen to form water and H_2S did not appear in the sulfur generator vent gas. The reaction of a part of the inlet hydrogen with chemisorbed oxygen had been observed in previous work and is apparently instrumental in retaining the activated carbon's activity upon cycling. As the hydrogen was increased from 4.3 to 4.6 a part of the product sulfur reacted to form H_2S which appeared in the vent gas, while formation of water essentially remained constant. The difference between the measured hydrogen input and output amounts to about 12% and could be the result of analysis error or, possibly, chemisorption of these small amounts of hydrogen on the carbon itself.

If the hydrogen ratio were lowered below that of Condition C, SO_2 formation would be expected at the expense of part of the sulfur product. This would be the desired direction if the process is slightly out of balance since SO_2 can be readily recycled to the sorber.

During these integral tests and with prior work, there was limited temperature control in the moving bed sulfur generator. As a result of higher than desired temperatures, a part of the sorbed acid decomposed to SO_2 in the upper part of the unit and was not readily available for conversion to sulfur. Thus a maximum of 85% conversion of the sorbed acid to sulfur was obtained with this equipment. Prior testing had shown that with proper temperature control essentially 100% conversion to sulfur is possible and this should be readily attainable in larger equipment where fluid beds will be used.

The gas residence time in the regenerators is only about 15 seconds; therefore, response of the system to hydrogen input is very rapid. Thus, control should be readily achieved by monitoring regeneration off-gases and adjusting the hydrogen input accordingly.

4.2.2 Detailed Integral Results

Detailed Operating Conditions and Results -

A detailed summary of the integral run conditions and results for both IR-1 and IR-2 is presented in Table 4. As can be seen, five steady state operating periods occurred during IR-1 and three during IR-2. All these periods represent changes in the regeneration conditions only. The SO_2 sorber conditions were maintained constant throughout. In periods 4, 5, 7 and 8, the ratio of hydrogen input to SO_2 sorbed (moles H_2/mole SO_2 sorbed) was deliberately changed to optimize the process for hydrogen consumption. Although the ratio of H_2/SO_2 sorbed is the same for Periods 7 and 8, Period 8 simulated the use of shifted producer gas for sulfur stripper/H_2S generator feed to evaluate its effect on carbon regeneration.

To evaluate the operating performance of the integral pilot plant, five performance variables--SO_2 removal, H_2S utilization, acid conversion to sulfur, H_2 utilization, H_2 utilization to H_2S-- were initially chosen as indicators. In the analysis of Runs 6, 7 and 8 where some of the acid was converted to sulfur in the sulfur stripper/H_2S generator, it became apparent that several other process responses might be more suitable for assessing integral operation.

Since the overall process response time to changes in process variables was not known, the attainment of steady state was taken to be when no variations about a statistical average were measured in the process streams. The data indicated that approximately 30 hours were required while using process H_2S before the total integral pilot plant reaches steady state after a change. In view of this, only Periods 3, 4 and 7 in Table 4 represent steady state conditions. Period 5 was very close to steady state,

Table 4. INTEGRATED OPERATING CONDITIONS AND RESULTS

	IR-1 RUNS					IR-2 RUNS		
STEADY STATE PERIOD	1	2	3	4***	5****	6	7	8
CYLINDER OR PROCESS H_2S	Cylinder	Cylinder	Process	Process	Process	Cylinder	Process	Process
TIME PERIOD (Hrs.)	34	12	37	55	16	25	61	8
CARBON RECYCLE RATE (Lbs./Hr.)	29	30	30	30	30	29	29	29
SO_2 SORBER*								
Conditions								
Gas Rate, CFH	15,800	15,800	15,800	15,800	15,800	15,000	15,300	15,400
Temp. (Avg.), °F	189	193	188	189	186	196	191	185
Outlet Gas Temp., °F	194	196	193	191	189	191	191	184
Inlet SO_2 Conc., ppm (Dry Basis)	2,020	1,982	2,108	2,240	2,280	2,100	2,060	2,030
Rate, CFH	29.3	28.8	30.6	32.5	32.4	29.2	29.2	29.0
Temp. (Range), °F	169-203	170-207	163-208	167-209	166-202	177-226	167-204	168-197
Results								
Outlet SO_2 Conc., ppm (Dry Basis)	100	142	123	131	139	60	90	80
Rate, CFH	1.5	2.0	1.8	1.9	2.0	0.8	1.3	1.1
Outlet Acid Loading, lb./lb. C	0.27	0.28	0.26	0.26	0.24	0.22	0.22	0.23
Pressure Drop, in. H_2O	25.3	25.7	26.7	28.5	33.0	25.2	26.4	26.3
SO_2 Removal, % Inlet	95	93	94	94	94	97	96	96
Carbon Attrition Rate, lb./hr.	0.36	0.33	0.31	0.29	0.28	0.35	0.28	0.28
CARBON CONDITIONER								
Conditions								
**Steam Conc., vol. %	61	61	61	100	100	100	100	100
Carbon Bed Temp. (Avg.), °F	317	321	319	321	325	324	320	324
Results								
Carbon Moist. Load., lb./lb. C	0.076	0.078	0.078	0.09	0.10	0.11	0.10	0.09
SULFUR GENERATOR								
Conditions								
Temperature C Bed (Range), °F	245-313	262-311	264-315	250-340	264-310	251-306	263-312	262-306
(Avg.), °F	268	289	291	292	288	279	289	287
Inlet N_2, CFH	175	175	190	165	175	106	121	87
Inlet H_2S, CFH	72	72	73	83	76	88	62	58
Inlet CO_2, CFH	0	0	0.9	0.9	0.8	0	1.0	40.9
Inlet Acid Load., lb./lb. C	0.27	0.28	0.26	0.26	0.24	0.22	0.22	0.23
Results								
Outlet Acid Load., lb./lb. C	---	---	0.03	0.012	0.016	0.008	0.034	0.04
Outlet S Load., lb./lb. C	0.30	0.29	0.29	0.29	0.28	0.29	0.21	0.21
Outlet H_2S, CFH	---	---	---	6.5	3.2	15.3	0.08	1.3
Outlet SO_2, CFH	---	---	---	2.2	2.7	2.1	3.8	4.4
Outlet CO_2, CFH	---	---	---	0.7	0.8	0	1.0	40.9
Outlet H_2O, CFH	---	---	---	160	170	122	135	126
H_2S Utilization, %	---	---	---	92	96	84	100	98
Acid Conversion to S, %	71	69	75	87	90	99	73	62
S Evol., Ratio to SO_2 Sorbed								
(as H_2S)	---	---	---	0.22	0.11	0.61	0.003	0.05
(as SO_2)	---	---	---	0.08	0.09	0.08	0.14	0.16
H_2S GENERATOR/SULFUR STRIPPER								
Conditions								
Temp. C Bed (Range), °F	591-1406	920-1428	918-1366	966-1382	1005-1353	542-1210	500-1300	500-1350
(Avg.), °F	1110	1168	1161	1205	1191	970	982	1027
**Inlet N_2, CFH	190	190	190	165	175	100	100	66
**Inlet H_2, CFH	87	114	114	128	116	95	95	95
**Inlet CO_2, CFH	0	0	0	0	0	0	0	40
Inlet S Load., # S as S/# C	0.30	0.29	0.29	0.29	0.28	0.29	0.21	0.21
# S as H_2SO_4/# C	---	---	0.03	0.012	0.016	0.008	0.034	0.04
Results								
Outlet S Load., #/# C	0.052	0.033	0.035	0.034	0.032	0.041	0.043	0.047
Outlet H_2, CFH	0	0	1.0	1.7	0	0	0	0
Outlet H_2S, CFH	57	73	73	88	74	77	62	58
Outlet SO_2, CFH	0	0	0	0	0	0	0	0
Outlet H_2O, CFH	25	38	41	32	37	20	44	45
Outlet CO_2, CFH	1.5	1.2	0.9	0.9	0.8	1.6	1.0	40.9
H_2 Util., % of Inlet	100	100	99	99	100	100	100	100
Conv. to H_2S, %	66	62	62	63	61	81	67	61
Ratio to SO_2 Sorbed	3.1	4.2	3.8	4.3	3.9	3.4	3.4	3.4
SULFUR CONDENSER								
Outlet Gas Temperature (Avg.), °F	278	274	270	269	259	273	274	270
S Recov., lbs./hr.	3.8	0.8	1.6	1.6	1.9	---	1.9	2.0
% of Stripped	52	11	21	19	22	---	32	35
% of SO_2 Sorbed								
(by S Recov.)	---	---	65	63	75	---	87	86
(by S Evolved in S Gen.)	---	---	---	71	80	---	86	60
Average	---	---	---	67	78	---	84	81

*All sorber conditions steady for whole run period of about 8 days or 13 cycles.

**Only condition changes during run.

***Gas sampling error found and rectified.

****At end of period H_2 leak was found.

and Period 8 was close enough to steady state to yield data indicative of overall process operation at the corresponding process conditions.

The data in Table 5 indicate a number of results obtained during the integral run. The SO_2 removal goal of 90% was exceeded with 93 to 97% obtained for all the carbon cycles in both tasks. The H_2S utilization was increased to 100% by lowering the H_2 to SO_2 sorbed ratio to 3.4, but as a result, the sulfuric acid conversion to sulfur was decreased in the sulfur generator. The overall sulfuric acid conversion to elemental sulfur, however, increased as the desired effect, as shown by the sulfur recovery increase. This means that the effective acid conversion was completed in the H_2S generator/S stripper. The H_2 utilization was 100% and

Table 5. PROCESS OPERATING PERFORMANCE

Performance of Process Unit	Goal	IR-1 Run		IR-2 Run	
		4	5	7	8
SO_2 Sorber					
SO_2 Removal, % of input	90	94	94	95	95
Sulfur Generator					
H_2S Utilization, % of input	95	92	96	100	98
H_2S Evolution, % of SO_2 removed in SO_2 sorber	--	21	11	0.3	5
SO_2 Evolution, % of SO_2 removed in SO_2 sorber	--	7	10	14	16
H_2SO_4 Conversion to Sulfur, %	99	87	90	70	60
H_2S Generator/S Stripper					
Ratio H_2/SO_2	--	4.3	3.9	3.4	3.4
H_2 Utilization, % of input	90	100	100	100	100
SO_2 Evolution, % of SO_2 removed in SO_2 sorber	--	0	0	0	0
Carbon Burn-off, lbs. C/T SO_2 sorbed	--	10	10	13	11
Sulfur Condenser					
Sulfur Recovery, % of SO_2 removed in SO_2 sorber	--	67	77	84	83

*Close approach to steady state in these regeneration periods. In Task IV-A, Period 3 simulated producer gas used.

H_2 utilization to H_2S decreased which would result from the increased acid conversion in the H_2S generator/S stripper or decreased recycle process H_2S. The decreased regenerant H_2S gas recycle is viewed as a benefit, since the H_2 utilization is maximized. In summary then, the overall intended goals were markedly improved in the IR-2-C run as reflected by the increased flue gas SO_2 recovery as elemental sulfur. Most of the additional SO_2 was evolved in the sulfur generator outlet and could be recycled back to sorber to effectively close the loop, with a resultant increase in SO_2 recovery as elemental sulfur.

It is felt that SO_2 evolution is a thermal effect which can be reduced by better temperature control in fluid bed sulfur generators planned in future development. In any case, to put this SO_2 evolution in perspective, the sulfur generator off-gas contains SO_2, H_2O, CO_2 and N_2, all typical components of flue gas. The total gas flow rate of this stream is about 250 to 300 cfh @ 70°F in this pilot equipment. The stream would be recycled back to the SO_2 sorber resulting in an increase of less than 2% in the gas volume.

An unexpected results, mentioned above, that was found during the integral runs was the distribution of the acid conversion to elemental sulfur reaction between the sulfur generator and sulfur stripper/H_2S generator. With the decrease in H_2 input, the acid conversion to sulfur decreased in the sulfur generator as shown in Table 5. But, the overall acid conversion to sulfur, as indicated by sulfur recovery, increased as a desired effect. This meant that the effective acid conversion was completed in the sulfur stripper/H_2S generator. More importantly, this acid conversion in the sulfur stripper/H_2S generator was accomplished without an attendant increase in carbon burn-off as might be expected at the 1000°F reactor temperature and no SO_2 was evolved indicating conversion of the unconverted sulfuric acid to elemental sulfur. Also accompanying this shift in acid conversion was a decrease in H_2 utilization to H_2S while maintaining 100% H_2 utilization. Such a decrease in the H_2S recycle is considered beneficial since the H_2S utilization is maximized.

A short run was made, Period 8, in which the effect of a simulated shifted producer gas or reformer gas on regeneration was evaluated. Although the run lasted only 8 hours and "true steady state" results were not obtained, the apparent general effects were:

1) H_2S production in sulfur stripper/H_2S generator decreased

2) Acid conversion to elemental sulfur in the sulfur generator was further decreased.

3) No SO_2 evolution from sulfur stripper/H_2S generator

4) No effect on H_2 reduction of flue gas SO_2 to elemental sulfur

5) Carbon burn-off constant.

Overall, the shifted producer gas had no deleterious effects on process performance.

Activated Carbon Performance -

One of the main intents of the integral runs was to evaluate the activated carbon performance over extended carbon recycle conditions. The carbon was recycled for about 29 cycles, of which 21 were under flue gas/regeneration gas conditions. Some of the indicators of carbon performance are SO_2 activity, carbon attrition, carbon burn-off, mean particle diameter, pore volume, surface area, and ash content. Throughout the 29 cycles, there was no indication of any adverse effects on the carbon performance.

SO_2 Removal -

Some of the indicators of SO_2 activity of the carbon are SO_2 removal efficiency, acid loading of the carbon, sulfur loading of the regenerated carbon, and relative SO_2 activity as determined by an independent bench scale SO_2 sorption apparatus. The SO_2 removal efficiency, acid loading of the sorber product and residual sulfur loading of the regenerated carbon are shown in Figure 9 for the IR-1 and IR-2 runs. For all 21 cycles, the SO_2 removal was above 90% and actually ranged from 93 to 97% for an inlet SO_2 concentration of 1850 to 2050 ppm SO_2 to yield a carbon loading of 22 to 26 lbs. acid/100 lbs. carbon from the sorber. In IR-2 the SO_2 removal average was higher but the inlet SO_2 concentration was slightly lower. The residual sulfur loading of the regenerated carbon was about 0.035 lb. sulfur/lb. carbon for IR-1 run and about 0.04 to 0.045 lb. S/lb. C for the IR-2 run.

It would be expected that this slightly higher residual sulfur loading might reduce the relative SO_2 activity. As seen by Figure 10, in which the relative activity is given, the activity was decreased slightly because of the slightly higher residual loading, but was relatively constant for the duration of IR-2 run. For the virgin precursor, the SO_2

Figure 9. Activated carbon performance during Westvaco SO_2 recovery integral pilot runs

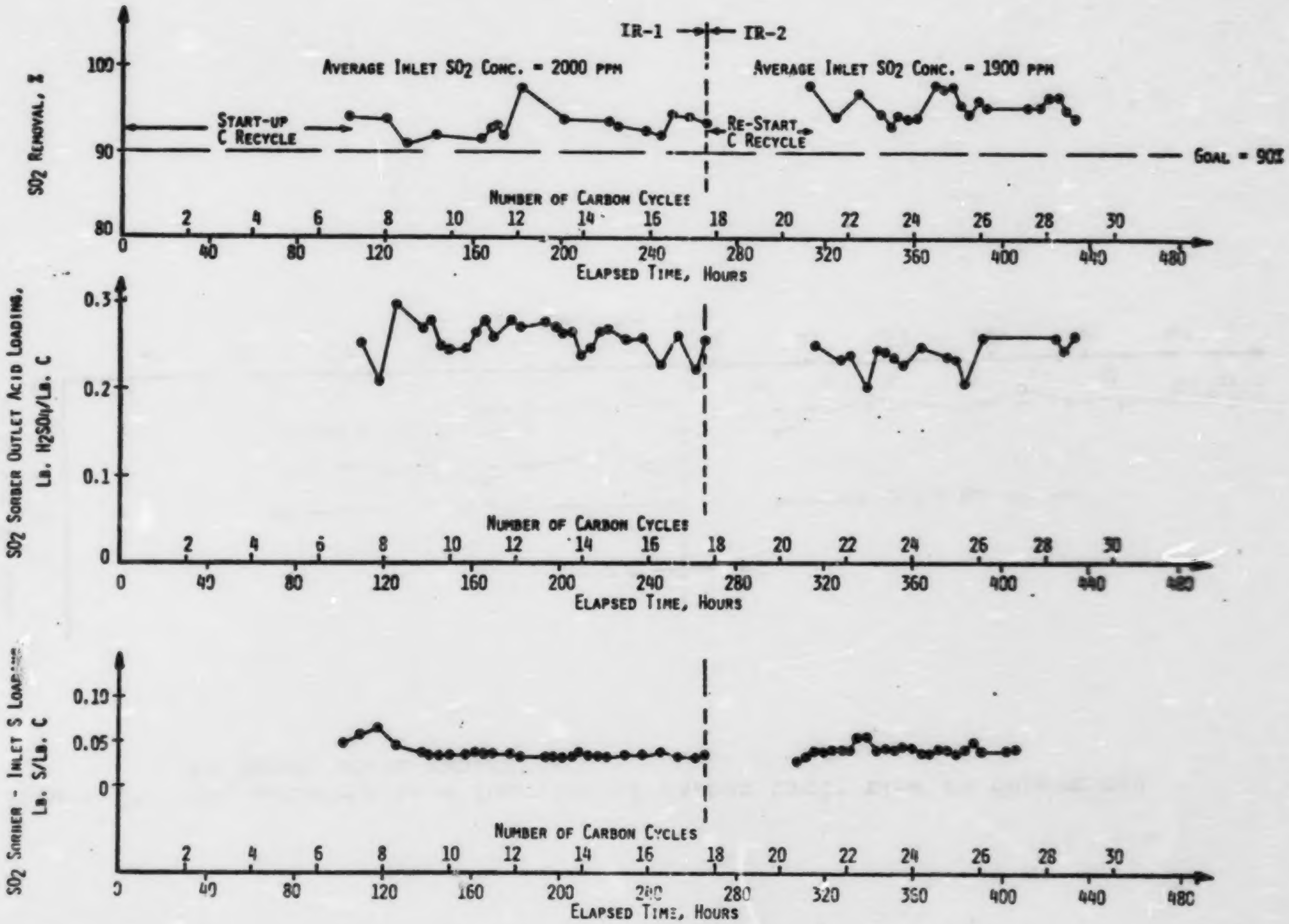
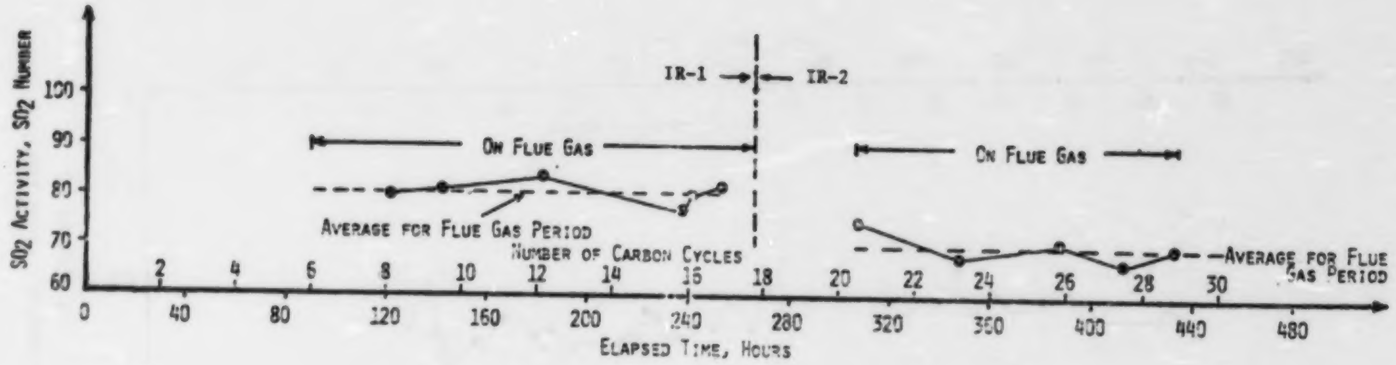


Figure 10. SO_2 activity as a function of carbon cycle time as determined by bench scale apparatus



number was 85 for comparative purposes. As shown in Table 4, the average temperature of the H2S generator/sulfur stripper was about 100 to 200°F lower than in the IR-1 run even though the intention was to operate under the same conditions as in IR-1. The reason was that the temperature controllers were set at a slightly lower temperature to prevent possible temperature overshoots experienced in the IR-1 run. It is expected, therefore, that the residual loading might be increased or the relative activity decrease, as was the case.

The switch from cylinder hydrogen to a simulated shifted producer gas had no apparent effect on the carbon's performance, as determined by the above measures of SO_2 activity.

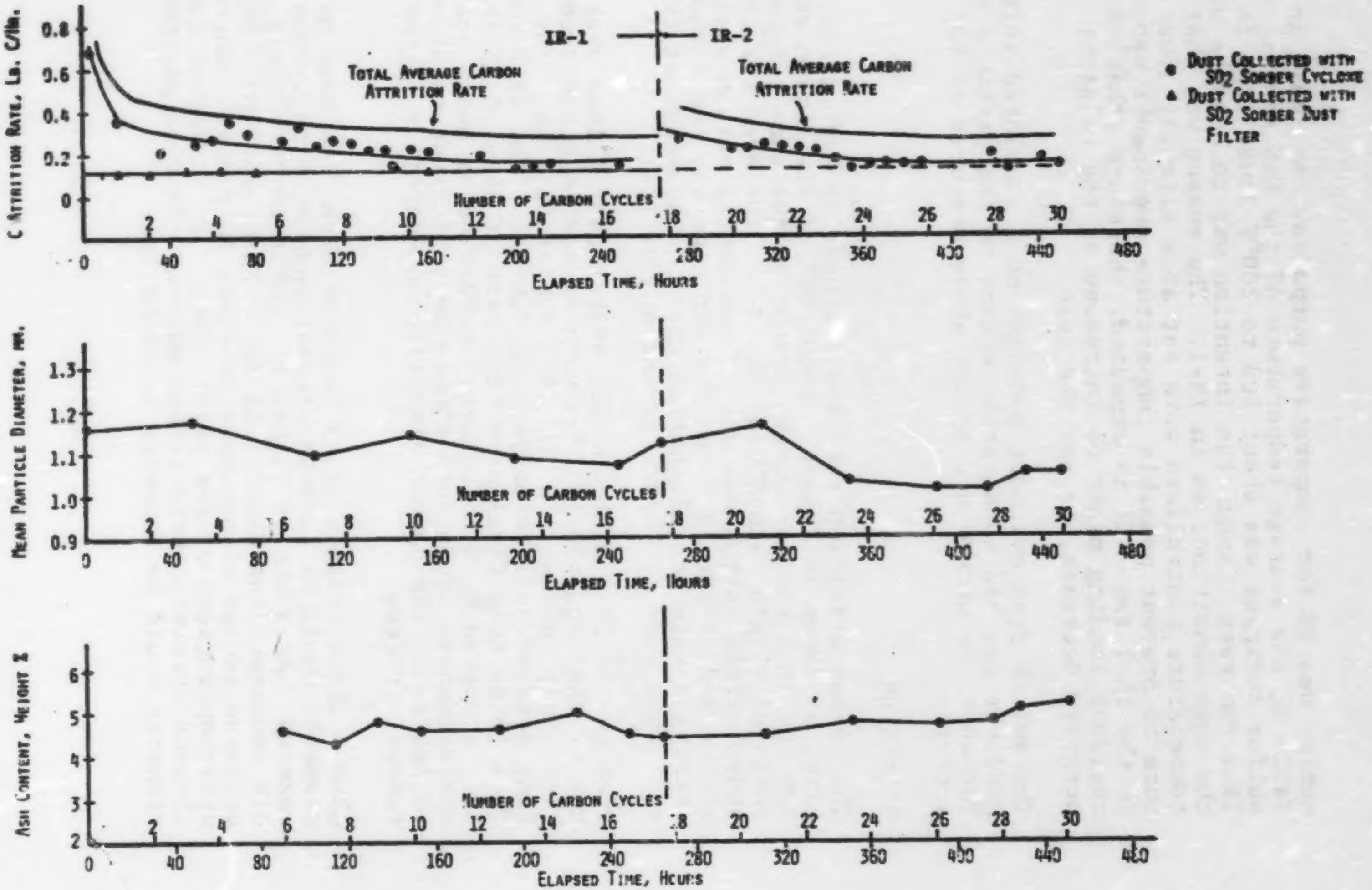
Attrition -

The carbon attrition rate was measured as a function of time, as shown in Figure. About 30% of the carbon charge for the IR-2 run was virgin carbon on the same original batch of virgin carbon used in IR-1. The need for this added virgin carbon was due to accidental carbon spillage at the end of the IR-1 run and explains why the carbon attrition rate was slightly higher at the start of the IR-2 run, than 0.27 lb. C/hr. at the end of IR-1.

Problems in IR-2 with the SO_2 sorber dust filter precluded use of that equipment. The rate of carbon collection was relatively constant in the IR-1 run at 0.12 lb. C/hr, so that rate of collection is also taken for the IR-2 run. This leads to a final attrition rate of about 0.25 lb. C/hr., compared to 0.3 lb. C/hr. predicted by bench scale measurements. This data should be sufficient to allow estimates of the carbon attrition on economics of the SO_2 removal process.

Also a direct result of carbon attrition, the mean particle diameter would be expected to decrease with no carbon make-up. As shown in Figure 11, the mean particle diameter did decrease from about 1.16 mm to about 1.05 mm. This decrease caused no apparent problems in process control or other operations of the pilot plant. In an actual continuous operation with carbon make-up, the mean particle diameter would be expected to stabilize.

Figure 11. Carbon attrition, mean particle diameter, and ash content as a function of carbon cycle time



Ash Content -

The carbon is exposed to flue gas each carbon cycle during which the carbon could pick up fly ash. Exposure for 21 cycles did not affect the ash content as shown by the relatively constant value in Figure 11. The ash content varied continuously between 4.4 to 5.2%, indicating no significant fly ash pickup.

Carbon Burn-off -

Throughout the runs in both IR-1 and IR-2, the inlet and outlet gas streams of the sulfur generator and H_2S generator/sulfur stripper are analyzed for H_2O, CO_2, CO, H_2S, H_2, N_2 and SO_2 with a process gas chromatograph. Presumably the difference between the CO_2 and CO content of the inlet and outlet gas streams is a measure of the carbon burn-off in these vessels. The detailed gas analyses are given in Appendix A-12. No carbon monoxide was detected in the off-gas of either vessel. Carbon dioxide, however, was detected in both off-gas streams during process H_2S gas recycle as shown in Figure 12 for the IR-1 and IR-2 runs.

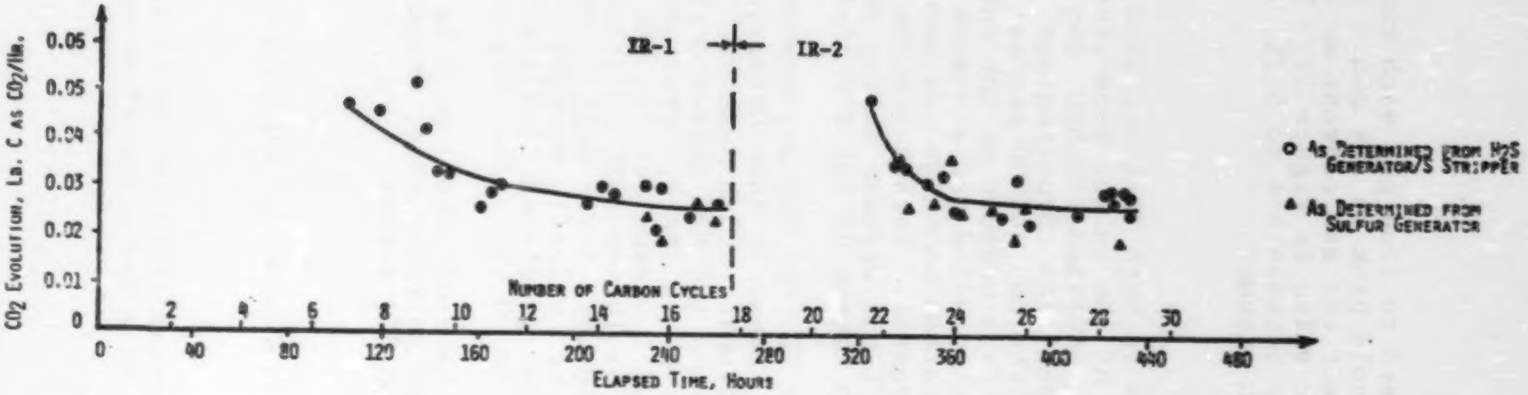
As seen from Figure 12, the CO_2 determined in the sulfur generator was about equal to that determined from the H_2S generator/S stripper, which necessarily implies that the burn-off occurs in the H_2S generator/S stripper. The carbon dioxide evolved in the H_2S generator/S stripper leveled off at about the same rate in the IR-2 run as the IR-1 run. The CO_2 evolution rate of about 0.026 lb. C as CO_2/hr. (or about 10 lbs. C/Ton SO_2) is apparently indicative of what might be typically expected. This burn-off rate agrees with that predicted from previous bench scale results of about 4 to 10 lbs. C/Ton SO_2 sorbed.

The maximum carbon burn-off that would be expected from reaction with sorbed sulfuric acid, Equation (9), is about 187 lbs. C/Ton SO_2 sorbed.

$$H_2SO_4 + 1/2\ C \longrightarrow 1/2\ CO_2 + SO_2 + H_2O \qquad (9)$$

The decrease in burn-off from 187 to 10 lbs. C/Ton SO_2 sorbed corresponds to a reduction of about 95%.

Figure 12. Carbon dioxide evolution as a function of carbon cycle time



Pore Volume and Surface Area -

The effect of repeated cycling of the carbon under process conditions on total pore volume and surface area was measured. Total pore volume and surface area which were determined for samples of regenerated carbon taken periodically during the two integral runs are shown in Figure 13. Because of the scatter in the data, which is within experimental error limits, the apparent slightly increasing nature of both the pore volume and surface area plots may not be considered statistically significant. Therefore, it appears that both the carbon's total pore volume and surface area were not appreciably changed with repeated exposure to sorption/regeneration conditions.

Regeneration -

Sulfur Generator -

The major indicators of the performance of the moving bed sulfur generator are the acid conversion to sulfur and H_2S utilization. The results obtained for these responses in this run are included in Figure 14. In comparing the two runs, IR-1 and IR-2, the H_2S utilization improved toward 100% utilization as the sulfur recovery increased. On the other hand, the acid conversion decreased to a steady value of about 70% since the increased H_2S utilization corresponded to a decrease in the stoichiometric quantity of H_2S recycled back to the sulfur generator. This decrease in acid conversion was accompanied by a slight increase in SO_2 evolution from the sulfur generator. However, it is felt that the SO_2 evolution could be reduced in fluid bed sulfur generators planned in future development since the fluid bed would offer more uniform temperature control. Moreover, the evolved SO_2 could be recycled to the SO_2 sorber with a minimal increase in load on the sorber. More importantly for the IR-2 run, the increased amount of acid entering the H_2S generator did not result in any SO_2 evolution from that reactor, indicating that the effective conversion of acid to elemental sulfur was completed in the H_2S generator.

As pointed out earlier in this report, the various performance goals were based partially on past performance of the various units operated separately. These goals may not be particularly representative of the performance of the integral process. Therefore, it is necessary to view the effect of these recent H_2S utilization and acid conversion to sulfur responses in terms of the overall process objectives, i.e. SO_2 removal, sulfur recovery, and H_2

Figure 13. Pore volume and surface area of recycled carbon

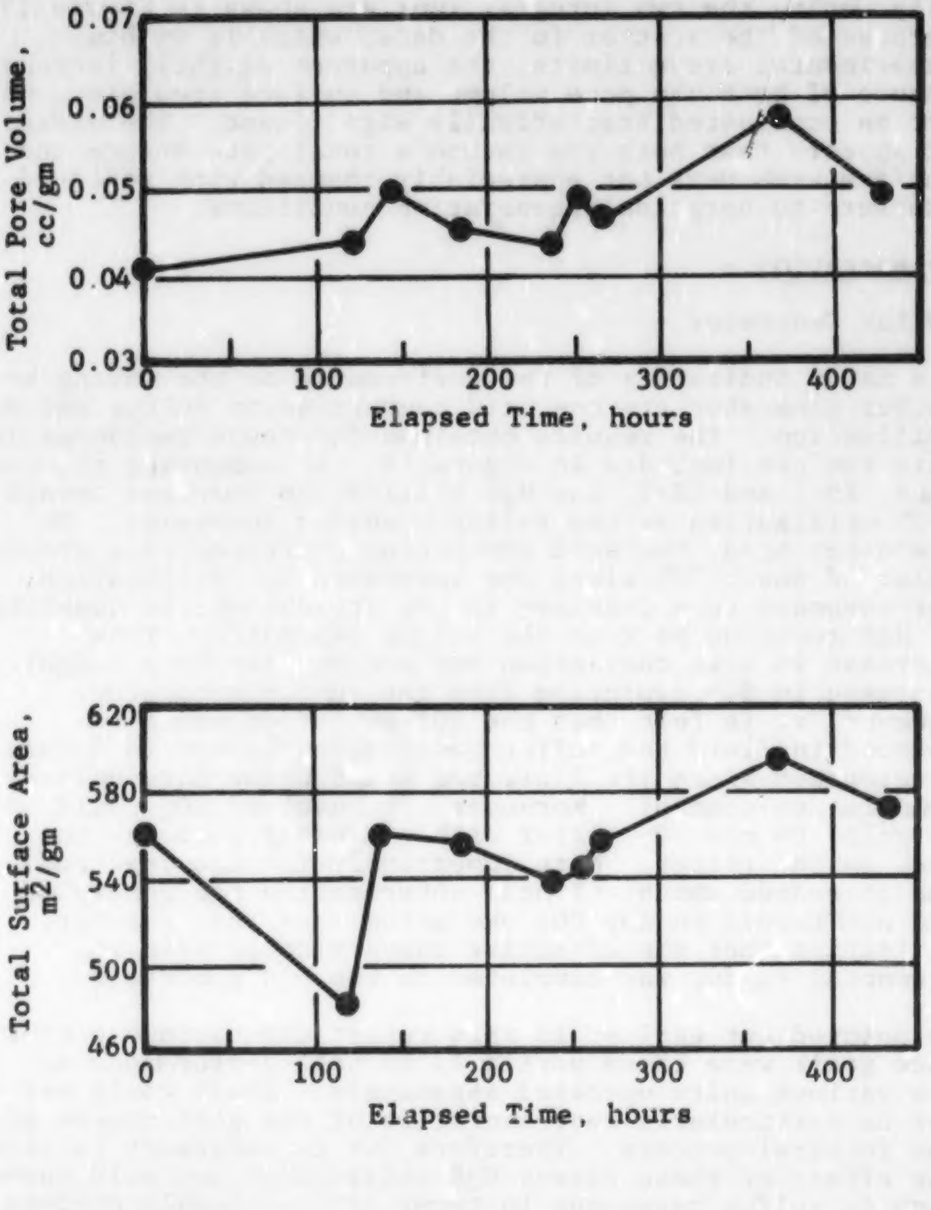
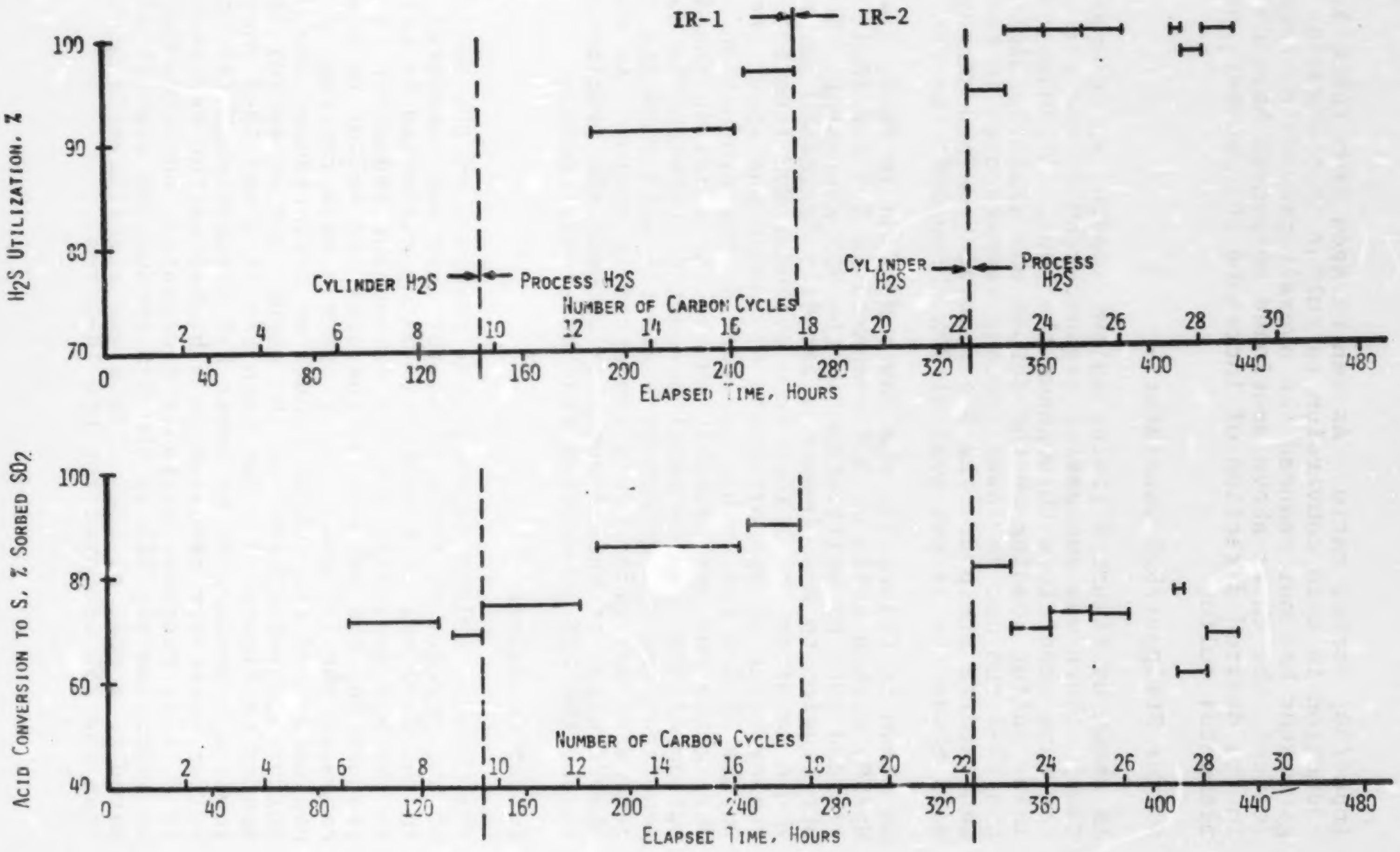


Figure 14. Sulfur generator performance



input/SO_2 sorbed ratio. As can be seen from Table 5, the reduction in acid conversion to sulfur in the sulfur generator has not reduced the overall process performance. In fact, the three above mentioned responses have changed in the desired direction of increased SO_2 recovery as elemental sulfur.

Sulfur Stripper/H_2S Generator -

As shown by Figure 9 (inlet sulfur loading vs. elapsed time), there was successful regeneration of the carbon to the same conditions throughout the runs. Although the inlet sulfur loading on the carbon was slightly higher in the IR-2 run due to lower average temperatures in the H_2S generator/S stripper, the SO_2 removal remained steady and well above the target goal of 90% throughout the run.

As shown in Figure 15, the lower H_2 feed in IR-2, i.e. a H_2/SO_2 sorbed ratio of 3.4 compared to 3.9 for IR-1, yielded 100% H_2 utilization in the H_2S generator. The H_2 utilization to H_2S, however, steadily decreased during the IR-2-A run after the switch from cylinder H_2S from 81% to a steady value of approximately 61% which was about the same in the IR-2-C run. This decrease in the production of H_2S during the run was probably due to the shift in the distribution of the acid conversion reaction between the sulfur generator and H_2S generator where the acid entering the H_2S generator was effectively converted to sulfur. As the distribution of this conversion between the reactors stabilizes, the H_2S production reached steady state.

Sulfur Condenser -

Previously, sulfur recovery was reported on the basis of the percent of stripped sulfur that was recovered. But in the IR-2 run with more acid being converted to sulfur in the H_2S generator and the subsequent reduction in H_2S production, the percent of the stripped sulfur recovered exceeded the 25% goal. To provide a more representative evaluation of the sulfur condenser performance, the percent sulfur recovered based on the amount sorbed as SO_2 is presented in Figure 16 for both the IR-1 and IR-2 runs. The lower H_2S production or lower H_2S breakthrough from the sulfur generator resulted in a higher sulfur recovery. For IR-2, this response variable fluctuated, but steadied out to approximately 88% as the H_2S production stabilized compared to a goal of 100%. This was significantly higher than the 75% achieved for the IR-1 run.

Figure 15. H2S generator/sulfur stripper performance

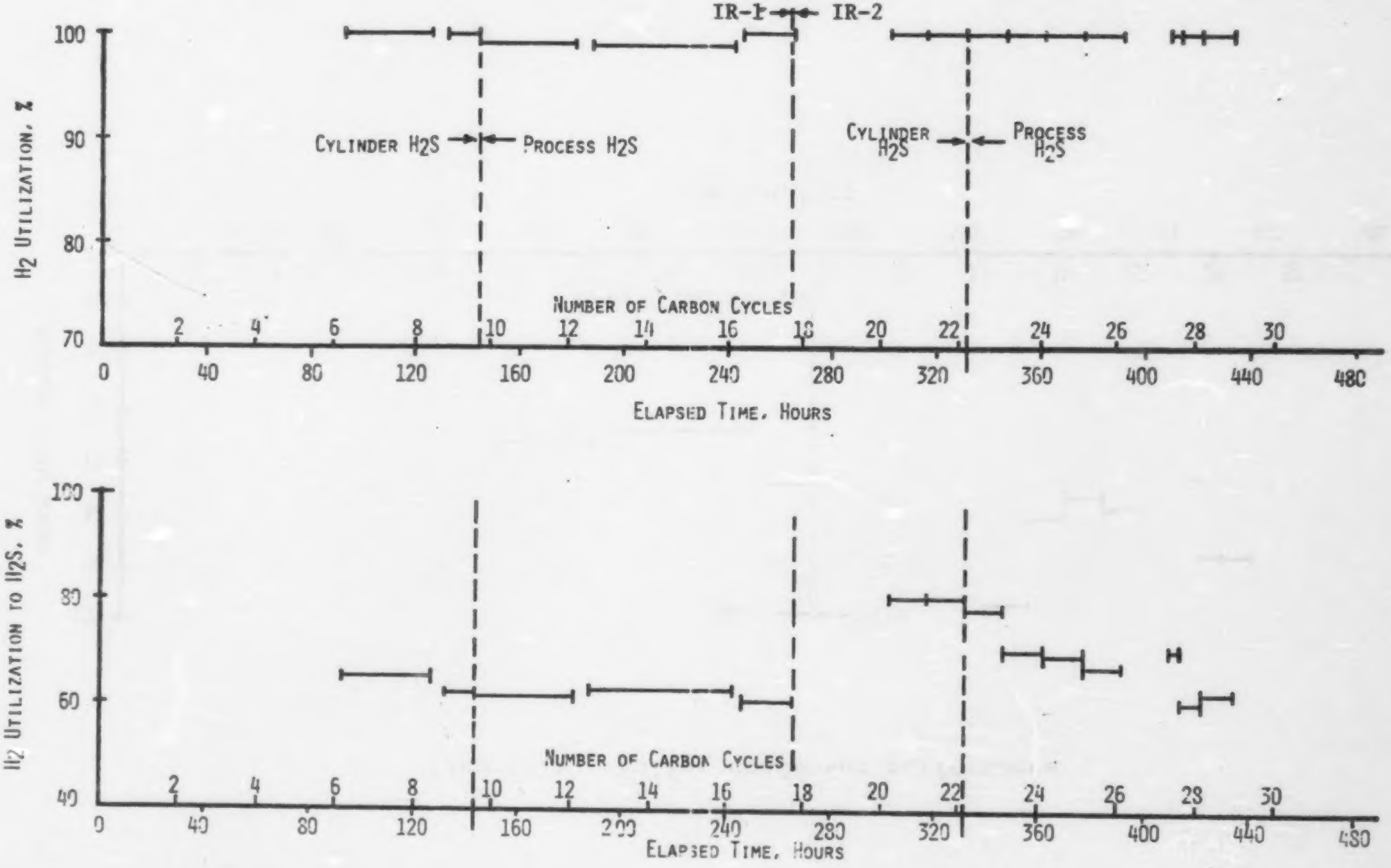
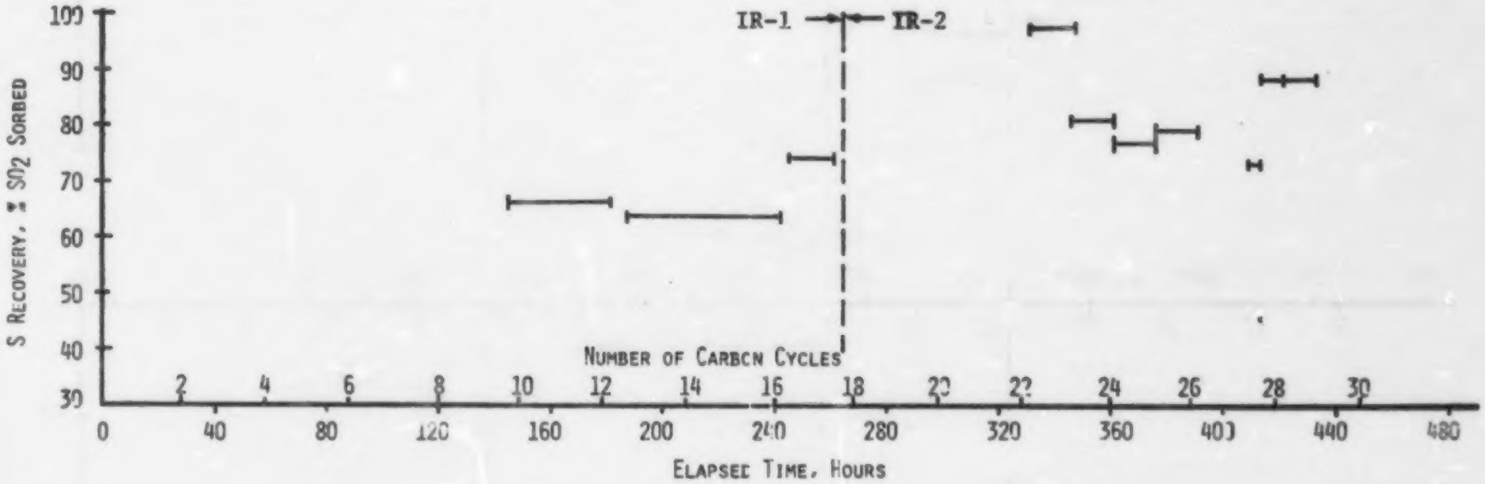


Figure 16. Sulfur condenser performance



4.2.3 Material Balances

Carbon Balance -

An attempt was made to perform a carbon balance in each of the integral runs; but, due to excess carbon spillage in the IR-1 run, only an overall carbon balance was made for the IR-2 run.

For the carbon balance that was determined for Run IR-2, the carbon loop was closed. At the start of the run the carbon fed to the reactors and inventory hopper was weighed carefully to determine the initial input to the system. Carbon leaving the system during the run as dust, leakage, or CO_2 was measured; and after completion of the run all material was removed from the system and weighed. Material weight was corrected for sulfur and moisture content to obtain the true weight of carbon. The carbon balance is presented in Table 6.

Table 6. CARBON BALANCE FOR IR-2 INTEGRAL RUN

IN	OUT
SYSTEM CHARGE = 428 LBS. C	CARBON REMOVED FROM INTEGRAL PILOT PLANT = 359 Lbs. C
	SO_2 SORBER CYCLONE = 31 Lbs. C
	SO_2 SORBER DUST FILTER* = 20 Lbs. C
	CARBON SAMPLES = 3.5 Lbs. C
	CO_2 EVOLUTION = 3.6 Lbs. C
	LEAKAGE AT BUCKET ELEVATOR = 6 Lbs. C
TOTAL IN = 428 Lbs. C	TOTAL OUT = 423 Lbs. C

*Based on constant rate of collection for the last steady state period in IR-1 run of 0.12 lb. C/hr.

Hydrogen Balance -

The hydrogen balance around the H_2S generator/S stripper is given in Table 7. The sources of hydrogen input were hydrogen in the inlet gas and hydrogen as adsorbed water and sulfuric acid on the incoming carbon. Hydrogen output consisted of H_2S, H_2 and H_2O in the outlet gas.

Table 7. HYDROGEN BALANCE FOR H_2S GENERATOR/SULFUR STRIPPER

Run	Period	H_2 Input, Lbs./Hr.		H_2 Output, Lbs./Hr.			Total, Lbs./Hr.	
		Gas - H_2	Carbon - H_2O	Gas - H_2S	Gas - H_2	Gas - H_2O	In	Out
IR-1	1	0.451	0.043	0.321	0	0.143	0.494	0.464
	2	0.591	0.048	0.409	0.002	0.214	0.639	0.625
	3	0.591	0.040	0.409	0.005	0.229	0.631	0.643
	4	0.663	0.015	0.480	0.01	0.194	0.678	0.684
	5	0.601	0.014	0.417	0	0.217	0.615	0.634
AVG.	158 Hrs.	0.587	0.029	0.416	0.005	0.196	0.616	0.617
IR-2	6	0.492	0.094	0.397	0	0.103	0.586	0.500
	7	0.492	0.140	0.332	0	0.233	0.632	0.565
	8	0.492	0.163	0.300	0	0.234	0.655	0.534
AVG.	113 Hrs.	0.492	0.132	0.343	0	0.190	0.624	0.533

For the IR-1 run, the difference between input and output averaged less than 1%. For IR-2, the hydrogen output averages 11% below the input. This 11% discrepancy could reasonably be attributed to experimental error in gas analyses, in flow rate measurements and in the inlet carbon moisture analysis. The measured carbon moisture content for IR-2 is higher than the theoretical value predicted by assuming that the water associated with the sulfuric acid on the carbon is at equilibrium between the gas and carbon phases on discharge of the carbon from the sulfur generator. Therefore, the 11% error in the H_2 material balance is considered within experimental error.

Sulfur Balance -

During the integral runs, the carbon and gas streams into and out of each vessel were monitored to obtain a total sulfur balance for each unit and for the total pilot plant. For the IR-1 integral run, there were five steady state periods. Two of the periods with cylinder H_2S gave an overall sulfur balance of IN/OUT of 8.65/8.93 and 8.31/6.41. Some recirculated sulfur was carried over into the sulfur product due to flooding of the mist eliminator in the sulfur condenser causing uncertainties in these balances. This was rectified and the overall sulfur balances with process H_2S were very good. The sulfur balances for the other periods are given in Table 8. Prior to the last two steady state periods, a problem with the sulfur analysis of the sulfur generator off-gas was rectified so the last two sulfur material balances should be very reliable. The sulfur balance IN/OUT ratios were 2.54/2.43, 2.70/2.64, and 2.78/2.57 as given in Table 8 for operation with process H_2S. This gave an average overall sulfur balance while on process H_2S of 2.64 lbs. S/hr. in and

Table 8. SULFUR BALANCE FOR INTEGRAL RUNS

Integral Run	Period	Input Sulfur SO_2 Sorber, lbs./hr.	Sulfur Outputs, lbs./hr.			Total Output, lbs./hr.	Input/Output Ratio
			SO_2 Sorber Off-Gas	Sulfur Gen. Off-Gas	Sulfur Cond. Product		
IR-1	3	2.54	0.19	--	1.58	--	--
	4	2.68	0.20	0.92	1.61	2.73	
	5	2.68	0.20	0.55	1.86	2.61	
IR-2	7	2.43	0.13	0.46	1.94	2.53	0.96
	8	2.40	0.16	0.38	1.94	2.48	0.99
Overall	87 Hrs.	2.42	0.14	0.31	1.85	2.30	1.05

2.56 lbs. S/hr. out for an average discrepancy of about 3%, or 97% of the sulfur in or out was accounted for. This indicates that especially for the Periods A and B, the conversion calculations and indicators of carbon performance are accurate.

An overall sulfur balance around the pilot plant system was calculated for the total period of process H_2S utilization during the IR-2 runs. The results of the sulfur balance are given in Figure 17. The amount of sulfur entering the sorber was 211 pounds and the amount leaving the sorber was 12 pounds, so that the amount sorbed which entered the regeneration system was 199 pounds. Of this, 27 pounds passed out of the system in the sulfur generator off-gas and 161 pounds was recovered in the sulfur condenser. This accounts for all but 11 pounds, or 5%, of the input sulfur, and this is probably within experimental error.

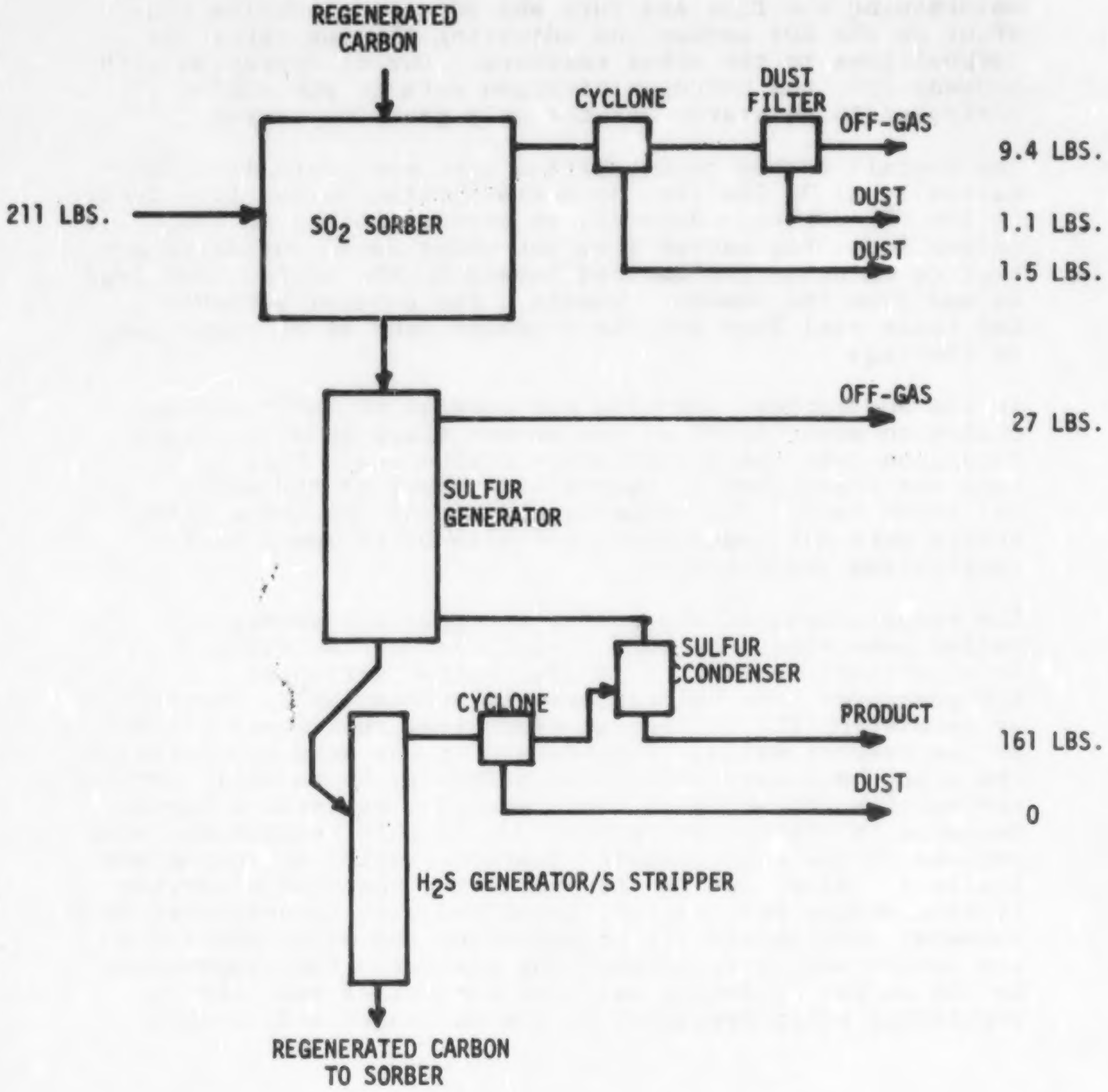
Twenty-eight pounds of sulfur which leaked out of the sulfur pump were collected after the run was over and included in the material balance as part of the 161 pounds of recovered sulfur, but the 28 pounds may not have accounted for the entire leak.

Sulfur balances for periods of operation with process H_2S during both the IR-1 and IR-2 runs are shown in Table 8. The results are presented as rates of sulfur input and output during each interval. Input consists of SO_2 adsorbed from the flue gas, and output is divided into three categories: 1) sulfur contained in the SO_2 sorber off-gas as SO_2 or sorbed on the carbon dust, 2) sulfur in the sulfur generator off-gas as SO_2 or H_2S, and 3) sulfur product collected in the condenser. The values for sulfur collection rate in the condenser have not been corrected for the sulfur leak, because of uncertainty in distribution the leak over the various periods. It is clear from Table 8, however, that the leak was worst during the periods from 81 to 126 hours, when the sulfur collection rate fell significantly.

4.2.4 Process Control

Overall process control of the integral pilot plant was achieved by a combination of automatic and manual control of critical process variables. Of these variables, only the temperatures of the SO_2 sorber's second stage and the sulfur stripper/H_2S generator, the overall carbon recycle rate, and the carbon levels in the seal legs of the reactors were under automatic control. The other variables, mainly gas rates and compositions, were controlled

Figure 17. Sulfur balance for IR-2 run during operation under process H_2S


REGENERATED CARBON
CYCLONE
DUST FILTER
OFF-GAS
9.4 LBS.
211 LBS.
SO_2 SORBER
DUST
1.1 LBS.
DUST
1.5 LBS.
OFF-GAS
27 LBS.
SULFUR GENERATOR
SULFUR CONDENSER
CYCLONE
PRODUCT
161 LBS.
DUST
0
H_2S GENERATOR/S STRIPPER
REGENERATED CARBON TO SORBER

TOTAL INPUT = 211 LBS.

TOTAL OUTPUT = 200 LBS.

manually on the basis of material balances and the process performance responses.

Manual control of the integral plant was accomplished by maintaining the flue gas rate and SO_2 concentration constant to the SO_2 sorber and adjusting the gas rates and compositions to the other reactors. During operation with process H_2S, the hydrogen/nitrogen rate to the sulfur stripper/H_2S generator was the only gas flow varied.

The overall carbon recirculation rate was controlled automatically at 30 lbs./hr. by a gravimetric solids rate feeder to the SO_2 sorber. However, at several points in the carbon loop, the carbon flow was under local automatic control to maintain the desired levels in the carbon seal legs to and from the reactor vessels. The control variable for these seal legs was the pressure drop of N_2 purge gas in the legs.

In the SO_2 sorber, the flue gas entered at 300°F and was cooled to about 175°F at the second stage by direct water injection into the second stage carbon bed. This temperature was maintained by automatic control of the water injection rate. The temperatures of the remaining three stages were not controlled, but allowed to reach their equilibrium temperatures.

The temperatures of the sulfur stripper/H_2S generator, sulfur generator, and sulfur stripper were maintained by electrical heating. In the sulfur stripper/ H_2S generator, the temperature was automatically controlled by regulating the current to electrical resistance heaters on the reactor walls. Temperature in the acid converter on the other hand were controlled primarily by manually setting the voltage rheostats to the electrical resistance heaters. Response to changes in temperature in this reactor was slow because of the heat transfer characteristics of moving bed reactors. Also, due to the exothermic reaction occurring in this moving bed reactor, localized over-temperatures were somewhat compensated for by adjusting the water content on the carbon before it entered the reactor. The temperature in the sulfur condenser was also controlled manually be regulating steam pressures to the exchanger and tracing.

4.2.5 Process Concept Modifications

Based on findings which arose at various stages in this development program, several modifications of the original process concept have evolved that not only have simplified process design and control requirements but also have reduced the capital and operating costs of the system. Briefly, these modifications involve:

1) **The method in which the flue gas temperature is controlled within the SO_2 sorber**

2) **The combination of sulfur stripping and H_2S generation into one process step**

3) **The fact that some of the acid can be reduced in the sulfur stripper/H_2S generator without deleterious effects on the process.**

In the SO_2 sorber, the first stage was operated at the stack gas temperature of approximately 300°F to remove the 30 to 50 ppm SO_3, and the second stage was operated at 175°F to facilitate SO_2 removal. The temperatures of the remaining fluid bed stages were not controlled, but were allowed to reach their equilibrium temperatures. To cool the flue gas between the first and second stages, an external shell and tube heat exchanger was installed and evaluated initially. The off-gas from the first stage was withdrawn from the sorber, circulated through the exchanger and returned to the sorber below the second carbon bed. Since certain design and economic constraints made this heat exchanger method of gas cooling particularly unattractive for large process units, direct water injection into the second stage fluid bed was installed. After the position of this water spray nozzle and the proper nozzle pressure were determined, this latter method was used satisfactorily during the integral runs and has been incorporated into the designs for the larger systems. As a result, the capital investment was reduced.

In the original process concept, the thermal stripping of the elemental sulfur from the carbon and subsequent partial reaction of this sulfur with hydrogen to H_2S were to be performed in separate process vessels. However, bench scale and pre-integral pilot plant testing indicated that these two process steps could be carried out satisfactorily in one reaction vessel, thereby appreciably simplifying the overall process. This process change was subsequently incorporated into the integral pilot plant as a fluid bed sulfur stripper/H_2S generator.

The design and operating conditions for the sulfur generator were selected initially to achieve 99% conversion of acid to elemental sulfur with maximum H_2S utilization. It was felt that this high level of acid conversion was necessary because the introduction of acid loaded carbon into the high-temperature H_2S generator could increase carbon burn-off and SO_2 evolution. During the integral runs, however, it was found that part of the acid on the carbon was reduced to sulfur in the sulfur stripper/H_2S generator without deleterious effects of SO_2 evolution or enhanced carbon burn-off. As a result the integral process can be operated with lower H_2S recycle and, consequently, without H_2S breakthrough from the sulfur generator. Moreover, reducing the amount of acid conversion in the acid converter should allow greater flexibility in process control.

SECTION 5
PRE-INTEGRAL PROCESS DEVELOPMENT

5.1 APPARATUS AND PROCEDURE

There were numerous types of reactors and procedures that were used in the process development. In general the studies can be classified by the type of reactor which included thermogravimetric, fixed bed, moving bed, batch fluid bed, and multistage fluid bed reactors. For each specific reactor type, the procedures are similar for studying the separate process steps and many of the procedures will thus be grouped as to reactor type.

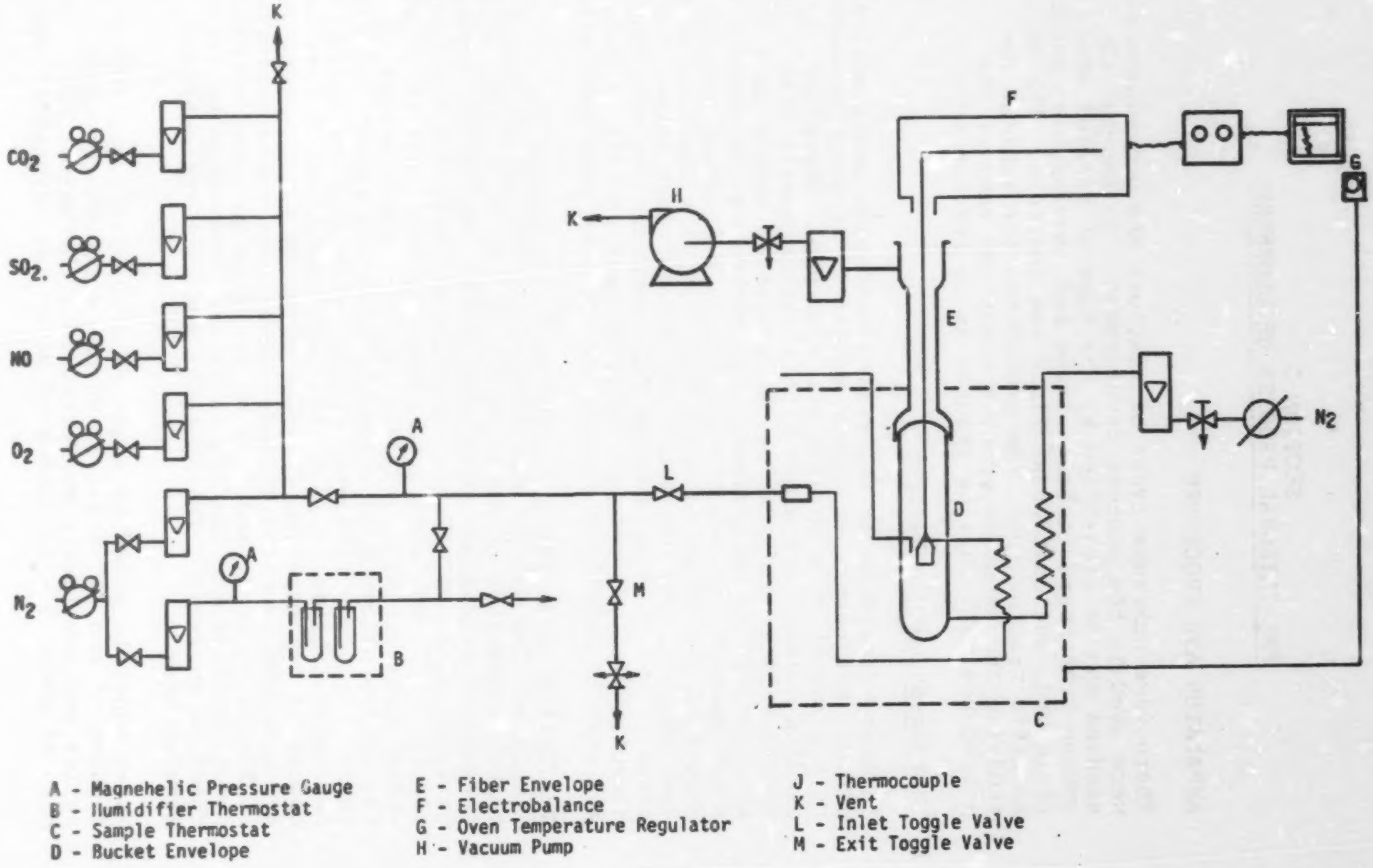
5.1.1 Thermogravimetric Reactor

In many adsorption or desorption processes using activated carbon, the change in carbon weight is directly proportional to the amount of a constituent adsorbed. Therefore, by suspending a small container with a carbon sample from a gravimetric balance and placing the suspended sample in a thermally controlled environment, the carbon can be exposed to a gas containing some constituent to be removed and the amount of pickup be followed directly as a function of time. Such an apparatus was assembled as described below, but since it was only used under this contract for studying the kinetics of SO_2 sorption, frequent mention will be made to SO_2 even though the equipment can be used more generally.

The apparatus is shown schematically in Figure 18. Simulated flue gas or some other suitable gas mixture is mixed by metering sulfur dioxide, nitric oxide, and nitrogen through individually calibrated Brooks "Sho-Rate" rotameters equipped with dual floats (steel and glass) and highly stable "ELF" nonrising stem needle valves. Use of these valves together with ordinary cylinder gas pressure regulators allows accurately reproducible setting of flow rates. In clean rotameter tubes, drift in flow indication has never exceeded 0.5% of the tube scale length over the course of any experiment. Flow rates in a convenient range are obtained by using cylinder gases containing approximately 1% SO_2 in N_2 or He and 0.3% NO in N_2 or He. Actual cylinder concentrations for the SO_2 tanks are determined by wet chemical analysis. The NO tanks are calibrated by the manufacturer.

Water vapor is added by means of a bubbler apparatus consisting of two 14" x 2-1/2" OD gas scrubbers connected in series and completely submerged in a thermostat bath. A head of about 6 - 10 inches of water was maintained above

Figure 18. Thermogravimetric apparatus


K
CO_2
SO_2.
NO
O_2
N_2
A
A
B
M
K
L
H
K
F
E
D
C
G
N_2
A - Magnehelic Pressure Gauge
B - Humidifier Thermostat
C - Sample Thermostat
D - Bucket Envelope
E - Fiber Envelope
F - Electrobalance
G - Oven Temperature Regulator
H - Vacuum Pump
J - Thermocouple
K - Vent
L - Inlet Toggle Valve
M - Exit Toggle Valve

the fritted dispersion tube in the first bubbler and about 2 inches in the second. Analysis of the gas effluent from the humidifier assembly using a Cambridge Systems dew point hygrometer has shown that saturation is achieved at all thermostat temperatures and carrier gas flow rates tested in the SO_2 sorption rate measurements.

The dry and humidified gas streams are mixed and then pass either to the sample or to a vent. This enables the simulated flue gas mixture to be completely mixed before introducing to the sample.

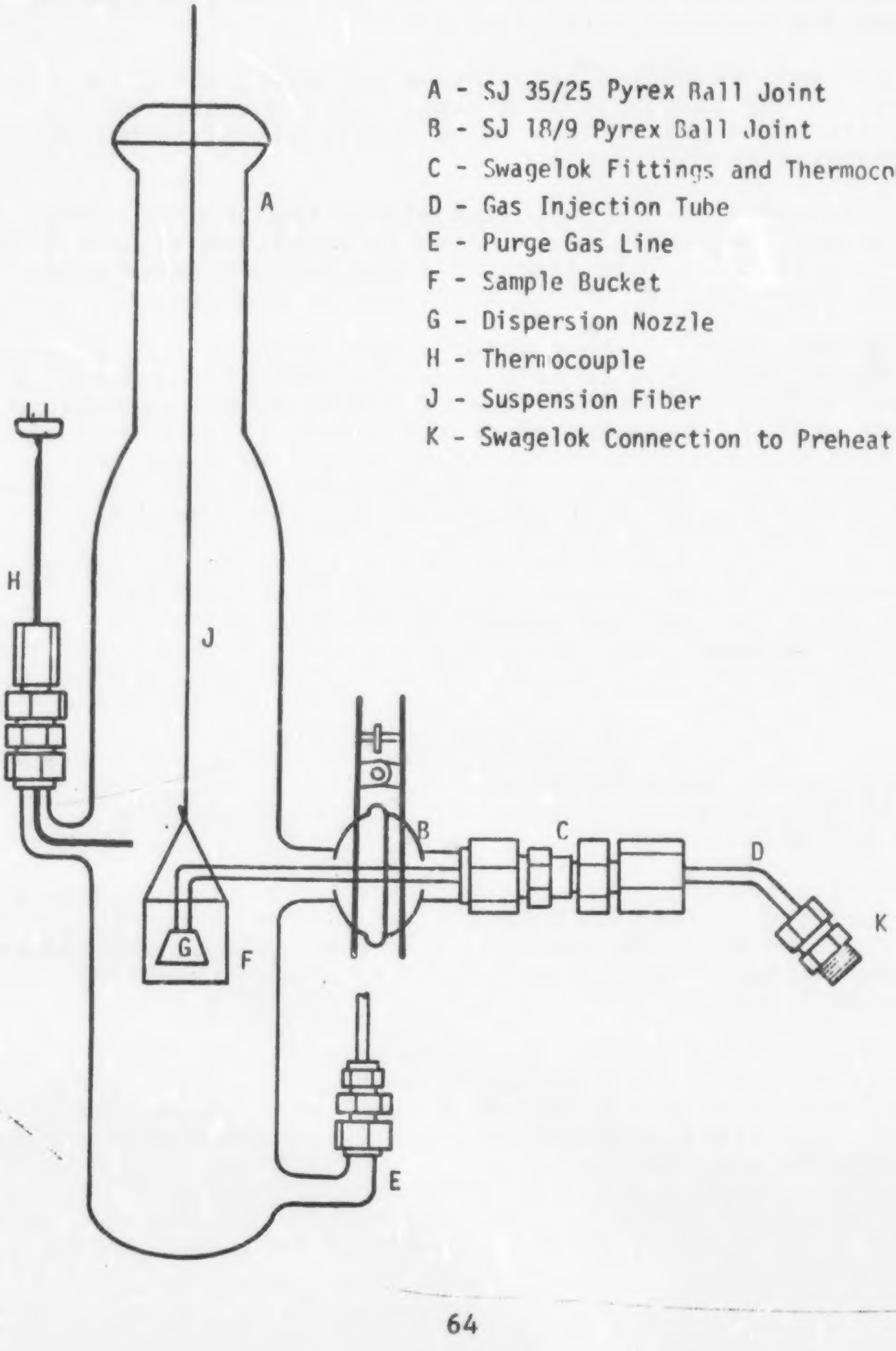
A needle valve in the vent line allows the pressure drop in the vent and sorption lines to be equalized so that flow may be switched at the start of a run without disturbance of pressures in the humidifier or the rotameters.

In the main part of the reactor, shown in detail in Figure 19, the carbon sample is held in a cylindrical fused silica bucket suspended from the beam of a Cahn RG electrobalance. The gas mixture is admitted to the sample through a nozzle positioned inside the bucket about 3 to 5 mm above the surface of the carbon layer. The nozzle was made of Teflon stock drilled to give dispersion of gas over the whole sample. Gas is conducted to the nozzle through a 1/16" stainless steel tube which passes through a Teflon sealed thermocouple gland attached by Swagelok fittings to a standard glass ball and socket joint which is sealed to the envelope in which the sample is suspended. Use of the gland and joint allows the lateral, rotary and angular motion required to position the dispersion nozzle within the bucket. The gas injection tube is connected to the gas mixing system by a coil of 15 feet of 1/16" SS tubing which allows preheating of the influent gas and provides sufficient flexibility to avoid undue strain on the glass-to-metal connections.

Also connected to the sample bucket envelope is a separate nitrogen purge line which is used to prevent air from entering the sorption apparatus after outgassing the sample and during the time that gas mixtures are being set up prior to a run.

The sample bucket envelope is removable so that samples may be changed and it is attached by a ball and socket joint to an upper tube which surrounds the bucket suspension fiber. The fiber envelope is about 14 inches long by 25 mm in diameter and contains a 3" section of 10 mm tubing at the upper end in order to prevent back diffusion of air into the sample section. Just above this construction, a side arm is attached which is connected to a Gast vacuum

Figure 19. Detail of the thermogravimetric reactor sample bucket envelope



A - SJ 35/25 Pyrex Ball Joint
B - SJ 18/9 Pyrex Ball Joint
C - Swagelok Fittings and Thermocouple Gland
D - Gas Injection Tube
E - Purge Gas Line
F - Sample Bucket
G - Dispersion Nozzle
H - Thermocouple
J - Suspension Fiber
K - Swagelok Connection to Preheat Coil

pump through a needle valve and rotameter. During a run, the flow through the vacuum system is maintained at such a rate that no corrosive or toxic gases are allowed to enter the atmosphere or the electrobalance mechanism case. Mixture with sufficient room air entering through the open top of the fiber envelope also prevents condensation of water from the gas mixture on the upper end of the fiber or in the vacuum system.

Reaction temperature is maintained by an air bath oven which is placed up around the reactor assembly and encloses the sample bucket envelope and the preheat coils attached to the gas injection and purge lines. The oven, which is very well insulated but weighs only about 10 pounds, was constructed in two parts. The bottom section was made from a 12" x 6" x 7" aluminum chassis box, insulated on the inside with 1/2" Fiberfrax ceramic fiber blanket. This section contains two 660 watt exposed coil heating elements and a centrifugal blower with an external fan cooled motor, The upper section, which formed the air bath, was constructed from 1/2" Fiberfrax blanket sandwiched between 9 mil corrugated aluminum sheeting. In operation hot air is blown out of the lower section, circulates through the air bath and returns through a 2-1/2" hole in the top of the heater chamber. Adequate temperature control is obtained using a Honeywell time proportioning controller with a thermistor sensor mounted in the outlet of the blower. Reaction temperature is measured by a thermocouple placed just above the sample bucket.

All lines coming into contact with water vapor are traced with electrical heating tapes to prevent condensation.

Weight pickup of SO_2 as sulfuric acid is measured by a Cahn RG electrobalance which is connected to a 10" Texas Instruments recorder to give a continuous readout of weight versus time. The sensitivity of the balance system is such that a full chart width deflection corresponds to a pickup of about 5 lbs. SO_2/100 lbs. carbon. In operation the flow of gases into the sample bucket causes a weight deflection corresponding to the flow rate. At the rate used in these experiments (1,000 cc/min.) the deflection is about 10 milligrams. Because the flow rates are very stable and reproducible, the deflection is always constant over the course of any experiment and the flow deflection can simply be subtracted from the observed weight changes due to SO_2 sorption. Gas flow around the bucket and suspension fiber also introduces a small amount of vibration into the weighing system. However the resultant noise band is less than 0.1 mg wide in most cases and had no effect on the accuracy of the measurements.

The weight pickup vs. time curves are differentiated by finding straight line slopes across closely spaced time intervals and plotting these rates vs. the mean loading in the corresponding interval.

5.1.2 Fixed Bed

The basic components of a typical fixed bed apparatus are shown schematically in Figure 20. The reactor, containing a known weight of carbon vertically oriented, typically has been 1" diameter. The reactor is equipped with a heating system consisting of electrical heaters wrapped around the pipe and a rheostat to control the heat input. Carbon temperature is measured with a thermocouple inserted into the carbon bed and gas temperature is also measured with a thermocouple. A gas mixing system provides control of reactant gas flows. Rotameters are used to measure the gas flow rates. The direction of gas flow is generally downward through the bed to avoid any possibility of fluidizing the bed. A gas chromatograph was used to monitor inlet and outlet concentrations of the gas constituents.

In operating a fixed bed system, the general procedure is to establish the desired inlet gas conditions with the gas bypassing the reactor, and to establish the desired carbon bed temperature with the heaters. When all conditions are set, the gas flow is switched to enter the reactor. The outlet gas is analyzed to give concentration vs. time data. The data from this type of experiment is transient rather than steady state. Outlet gas concentrations change continuously and eventually approach the inlet concentractions. Following the run the carbon is removed and analyzed for sulfur compounds.

The data can be analyzed to provide screening information on overall degree and rates of conversion and type type of reactor was used to study each of the process reaction steps.

5.1.3 Moving Bed

The main features of a moving bed system are shown schematically in Figure 21. There are many similarities to the fixed bed, including the systems for gas mixing, reactor heating, and gas analysis, the vertical reactor orientation, and the fact that the carbon beds are not fluidized. The main differences are that the moving bed reactor is a continuous flow system which operates under steady state conditions and the direction of gas flow is upward through the bed in

Figure 20. Fixed bed reactor system

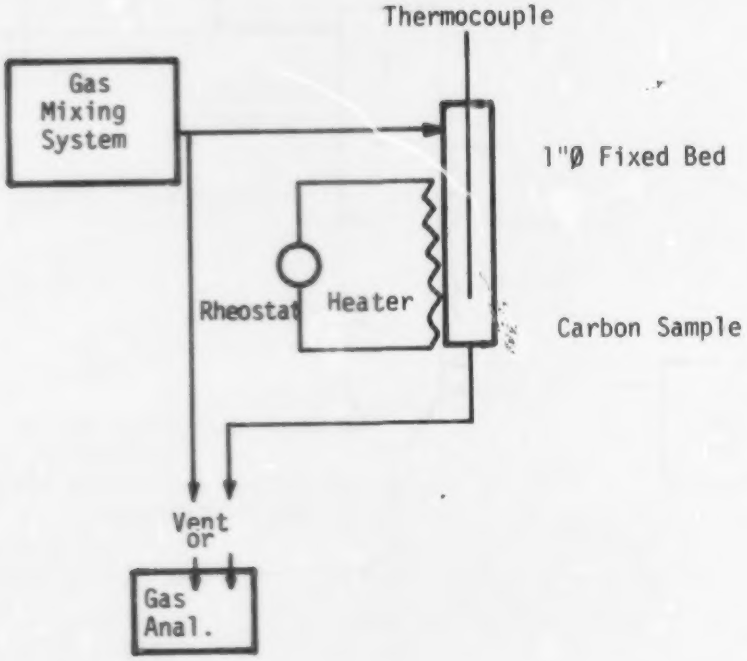
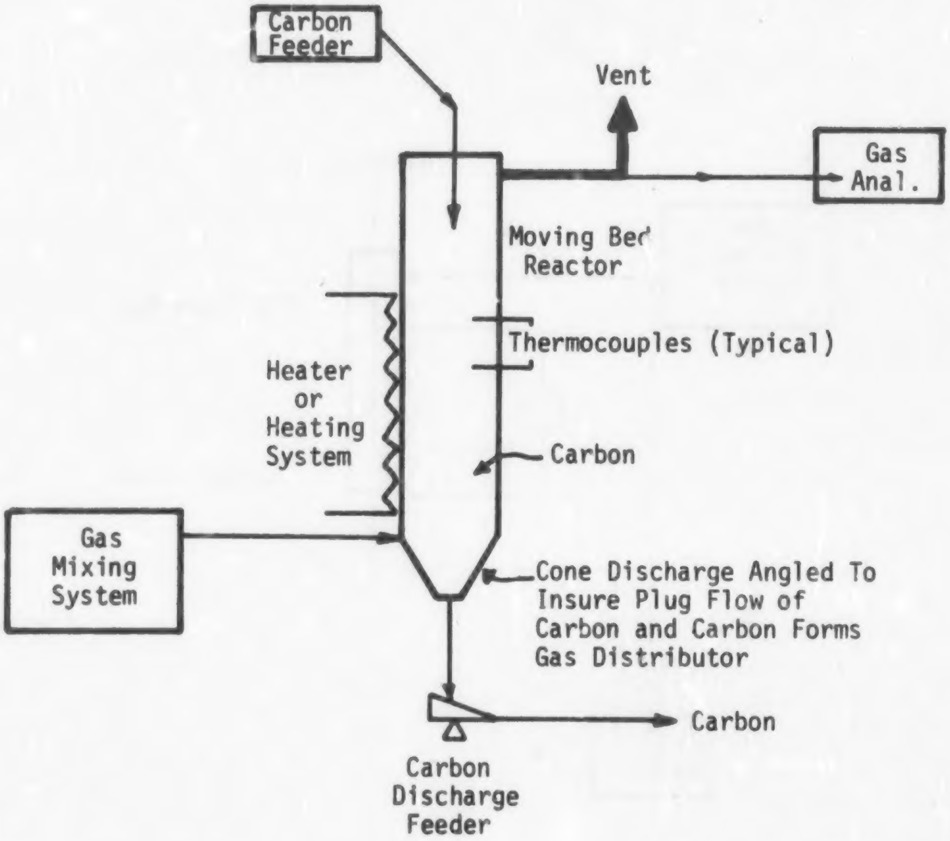

Thermocouple
Gas Mixing System
1"0 Fixed Bed
Rheostat
Heater
Carbon Sample
Vent or
Gas Anal.

Figure 21. Moving bed reactor system


Carbon Feeder
Vent
Gas Anal.
Moving Bed Reactor
Thermocouples (Typical)
Heater or Heating System
Carbon
Gas Mixing System
Cone Discharge Angled To Insure Plug Flow of Carbon and Carbon Forms Gas Distributor
Carbon
Carbon Discharge Feeder

order to provide countercurrent contact with the carbon phase. In addition, the moving bed requires a carbon flow control system to maintain the desired carbon flow rate through the reactor. Carbon feeders are used at both the inlet and outlet of the reactor. The carbon flow distribution through the reactor is close to theoretical plug flow.

The moving bed reactor is subject to temperature control problems as the vessel size increases due to poor heat transfer characteristics. Its main advantage is the capability for a long carbon residence time and low gas space velocity, two parameters which are important in obtaining high conversion of reactants.

Low gas space velocities can be obtained in a moving bed because the minimum fluidizing velocity constraint which applies to a fluid bed reactor is not applicable in a moving bed.

A bench scale (1-1/2" dia.) and pilot (8" dia.) moving bed reactor were used to study the conversion of sulfuria acid to sulfur by reaction with H_2S. Other reaction steps were not studied in the moving bed equipment.

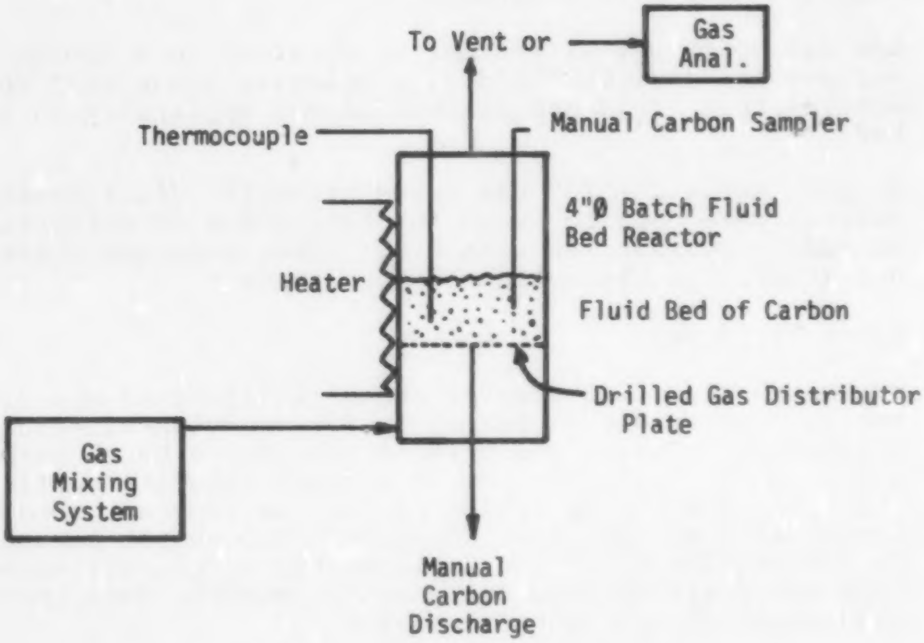
5.1.4 Batch Fluid Bed

The batch fluid bed reactor shown in Figure 22 is a differential reactor useful primarily for studying kinetics of a reaction. The approach is to fluidize a batch carbon sample with a reactant gas at a space velocity sufficiently high that the concentration of the gas reactant remains essentially unchanged as it passes through the carbon bed. Carbon samples are taken from the bed at closely spaced time intervals and are analyzed to generate data that is convenient for a kinetic analysis.

The equipment consists of a cylindrical vessel with a gas distributor plate to support the carbon bed. Electrical heaters provide heat input through the walls and are controlled manually with a rheostat. Temperature can be controlled accurately and is uniform throughout the bed because of the excellent heat transfer and mixing characteristics of the fluidized bed. A gas mixing system provides the desired gas flow rate and constituent concentrations, and the gas is introduced below the distributor plate.

A 4 inch diameter reactor of this type was used to develop a model for the reaction of acid with H_2S to form elemental sulfur and to study the thermal stripping of sulfur.

Figure 22. Batch fluid bed reactor


To Vent or
Gas Anal.
Thermocouple
Manual Carbon Sampler
4"Ø Batch Fluid Bed Reactor
Heater
Fluid Bed of Carbon
Drilled Gas Distributor Plate
Gas Mixing System
Manual Carbon Discharge

5.1.5 Multistage Fluid Bed Reactor

A multistage fluid bed reactor system is shown in Figure 23. Carbon is fed at a constant rate onto the top stage of the reactor and flows by gravity from one stage to the next. Gas distributor plates support the carbon beds. The plates are drilled to a specified percent open area, typically 8% with 0.125" dia. holes. The expanded bed depth, determined by the height of the overflow weirs, is generally limited to a value equal to the vessel diameter in order to minimize slugging of the bed. Downcomers extend into the carbon beds to within about 1-1/2" of the distributor plates. The downcomers contain baffling to prevent slugging and improve the carbon flow characteristics. Carbon passes out of the reactor into a seal leg designed to prevent the escape of any reactant gas. The carbon level in the seal leg is controlled automatically.

Reactant gas enters below the bottom distributor plate and passes upward through the reactor, countercurrent to the carbon flow. The gas is sampled for analysis at the inlet and outlet of the reactor, and may also be sampled at each stage of the reactor.

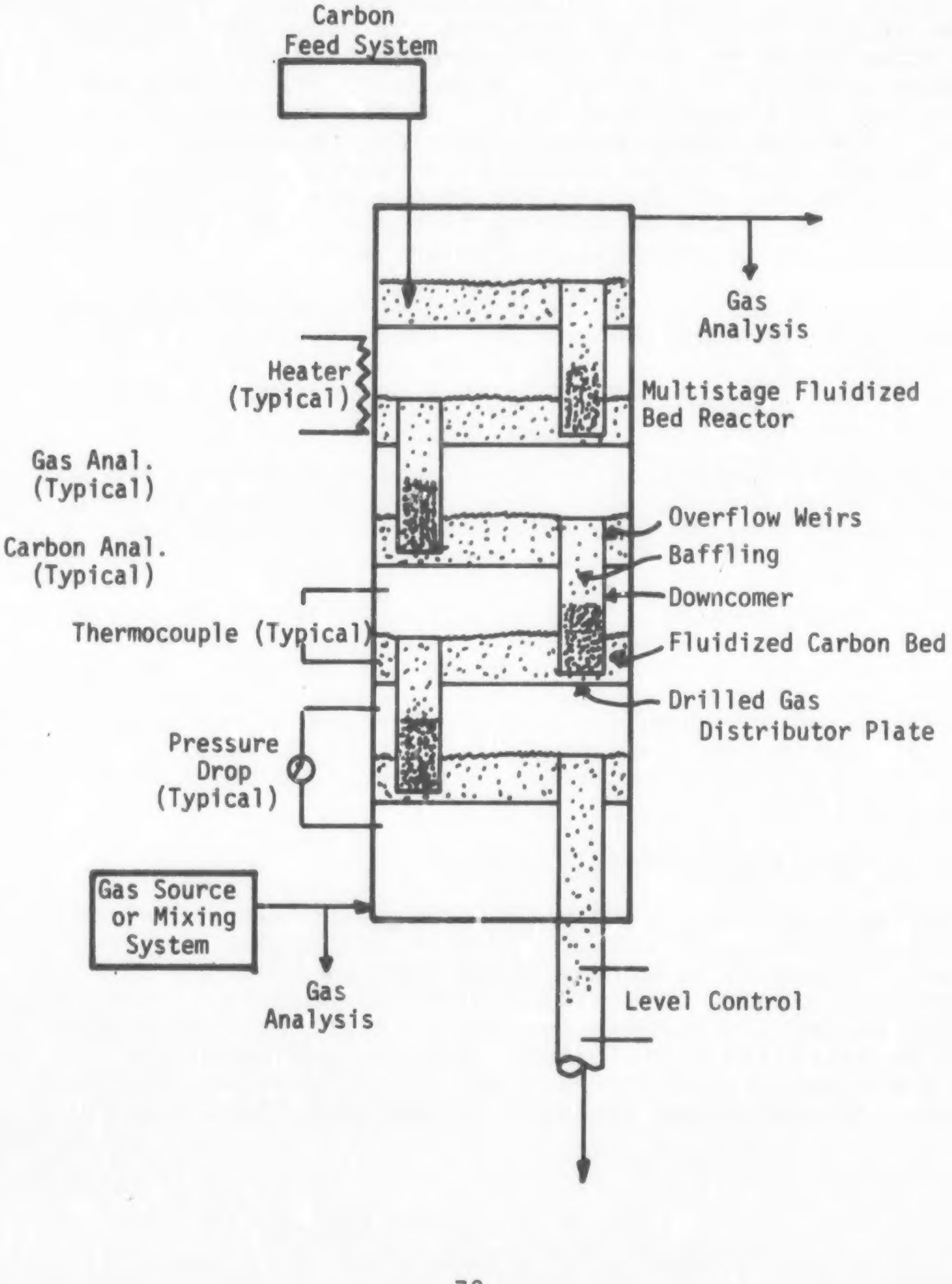
Temperature is controlled by electrical heaters wrapped on the outside of the reactor. Separate temperature control is frequently provided for each stage or for every two stages.

The multistage fluid bed reactor operates at steady state conditions. The time needed to reach steady state after start-up or after a change in operating conditions may be fairly long; however, so this type of reactor is not generally used in extensive kinetic studies. Multistage fluid bed units ranging from 4 - 18 inches in diameter were used to study the separate reaction steps and for thermal sulfur stripping.

5.1.6 Sulfur-Carbon Thermal Equilibrium

Adsorption isotherm points were obtained by saturating an inert gas stream with sulfur vapor at particular temperatures in order to produce a known partial pressure of sulfur, and passing this stream over carbon held at the desired adsorption temperature for a length of time sufficient to establish equilibrium. Sulfur loading on the carbon was determined for each set of equilibrium conditions by means of combustion analysis of the individual samples.

Figure 23. Multistage fluidized bed reactor


Carbon Feed System
Gas Analysis
Heater (Typical)
Multistage Fluidized Bed Reactor
Gas Anal. (Typical)
Carbon Anal. (Typical)
Overflow Weirs
Baffling
Downcomer
Thermocouple (Typical)
Fluidized Carbon Bed
Drilled Gas Distributor Plate
Pressure Drop (Typical)
Gas Source or Mixing System
Gas Analysis
Level Control

The apparatus used is shown diagramatically in Figure 24. In operation about 0.5 gm. of carbon sample was introduced, and after purging with nitrogen, the vapor generator and adsorption tubes were heated to the desired temperatures by manual control of Variac transformers. Nitrogen flow through the apparatus was maintained at a rate (10 cc/min.) low enough to attain saturation in the relatively inefficient generator. Connecting tubing between the generator and adsorber was heated to a temperature above that of the sulfur in order to prevent condensation. The exit tube at the bottom of the adsorber was also heated down to a condensation trap which was used to prevent sulfur from plugging the exit line. Nitrogen was injected into the line at this point in order to seal against entry of air from the exit.

After an equilibrium time of 9-1/2 hours which was set based on observations during the first experiment in which the highest sulfur pickup was achieved, gas flow through the generator was shut off. The stopcock between generator and adsorber was closed, and the entire apparatus was removed from the furnaces and allowed to cool. The carbon was then weighed, avoiding contact with atmospheric moisture, and the sulfur loading of the entire sample determined using a Dietert Sulfur Analyzer.

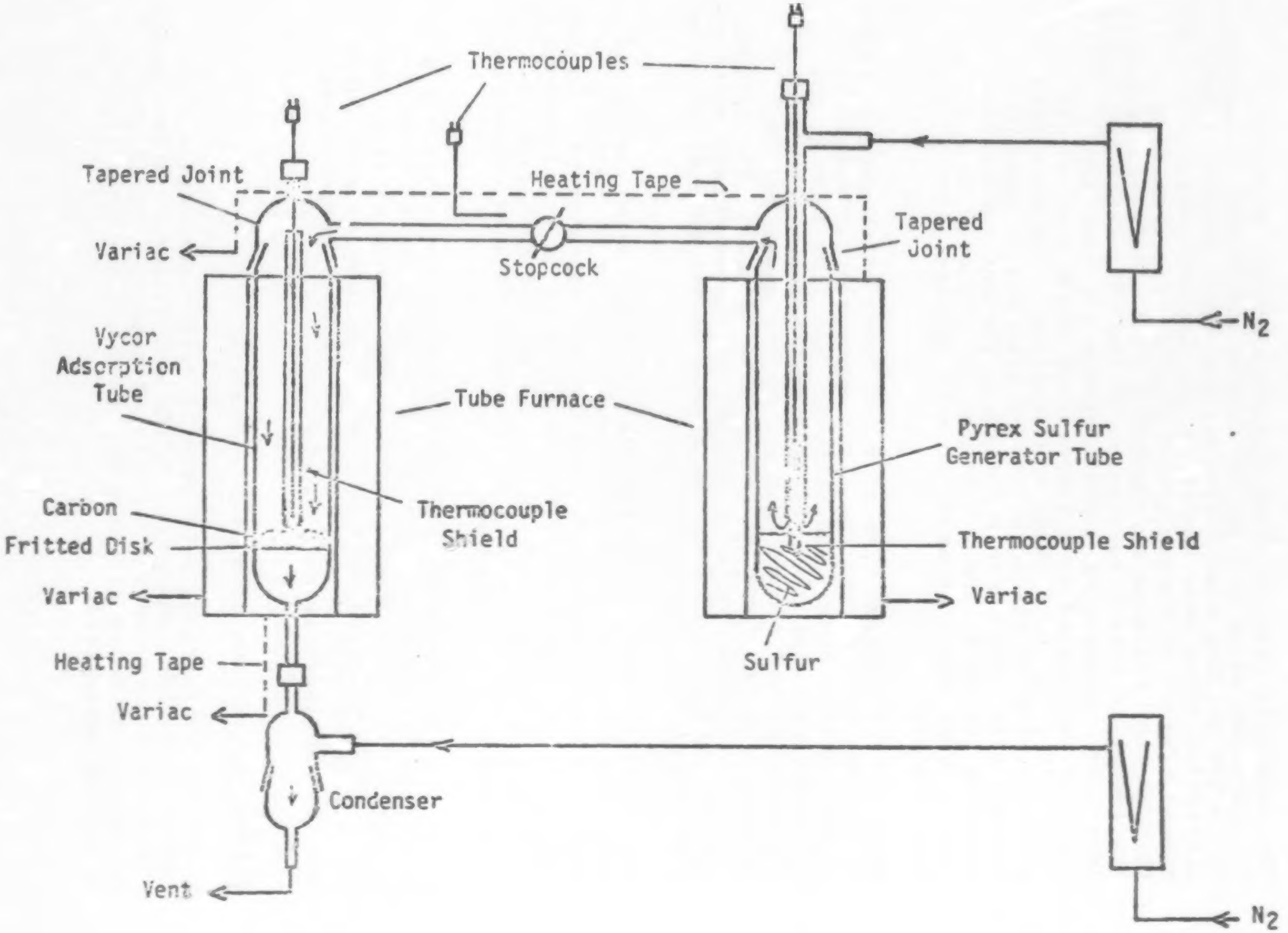
The carbon starting material used in these experiments had initially been loaded with about 24% sulfur by complete reduction of H_2SO_4 in sulfur generation experiments. Carbon having an initial sulfur load was used in order to reproduce adsorbent properties due to SO_2 pickup and reduction in accordance with our intent to use these data in connection with thermal stripping work.

Since the existence of chemisorbed sulfur on carbon has been suggested by previous thermal stripping studies in which a residual loading remained after extended purging with inert gas, additional runs were made in which samples were purged for 9.5 hours with pure nitrogen at several temperatures and then analyzed as noted above.

5.1.7 Solvent Extraction of Sulfur Procedures

Screening evaluations were made of sulfur extraction with carbon disulfide, ammonium sulfide and xylene by successive stages of slurry contact in stirred beakers. Since the procedures differed slightly for each solvent they will be described separately.

Figure 24. Sulfur adsorption apparatus


Thermocouples
Tapered Joint
Heating Tape
Variac
Stopcock
Tapered Joint
Vycor Adsorption Tube
Tube Furnace
Pyrex Sulfur Generator Tube
Carbon
Fritted Disk
Thermocouple Shield
Thermocouple Shield
Variac
Variac
Sulfur
Heating Tape
Variac
Condenser
Vent
N2
N2

Carbon Disulfide Extraction -

Twenty grams of a sulfur loaded carbon were slurried in a vertical stoppered flask for about 0.5 hr. at room temperature. The solvent was then decanted and evaporated to recover the dissolved sulfur for weighing. A fresh quantity of solvent was added and the procedure repeated to the desired number of extraction stages. After the final extraction the carbon was freed of excess solvent on a steam bath and then oven dried. Samples of the carbon were also taken at the end of each extraction stage, dried and analyzed for sulfur.

Ammonium Sulfide Extraction -

Forty grams of sulfur loaded carbon were slurried in a beaker at room temperature with 100 ml. of 20% ammonium sulfide for 15 minutes. The ammonium sulfide solution was then filtered off and the slurrying repeated with 100 ml. of fresh solution. After each stage of extraction a carbon sample was taken, slurry washed with water to remove excess ammonium sulfide, oven dried and analyzed for sulfur. The extraction solutions after each stage were acidified and boiled to liberate recovered sulfur which was then reclaimed through carbon disulfide extraction and dried.

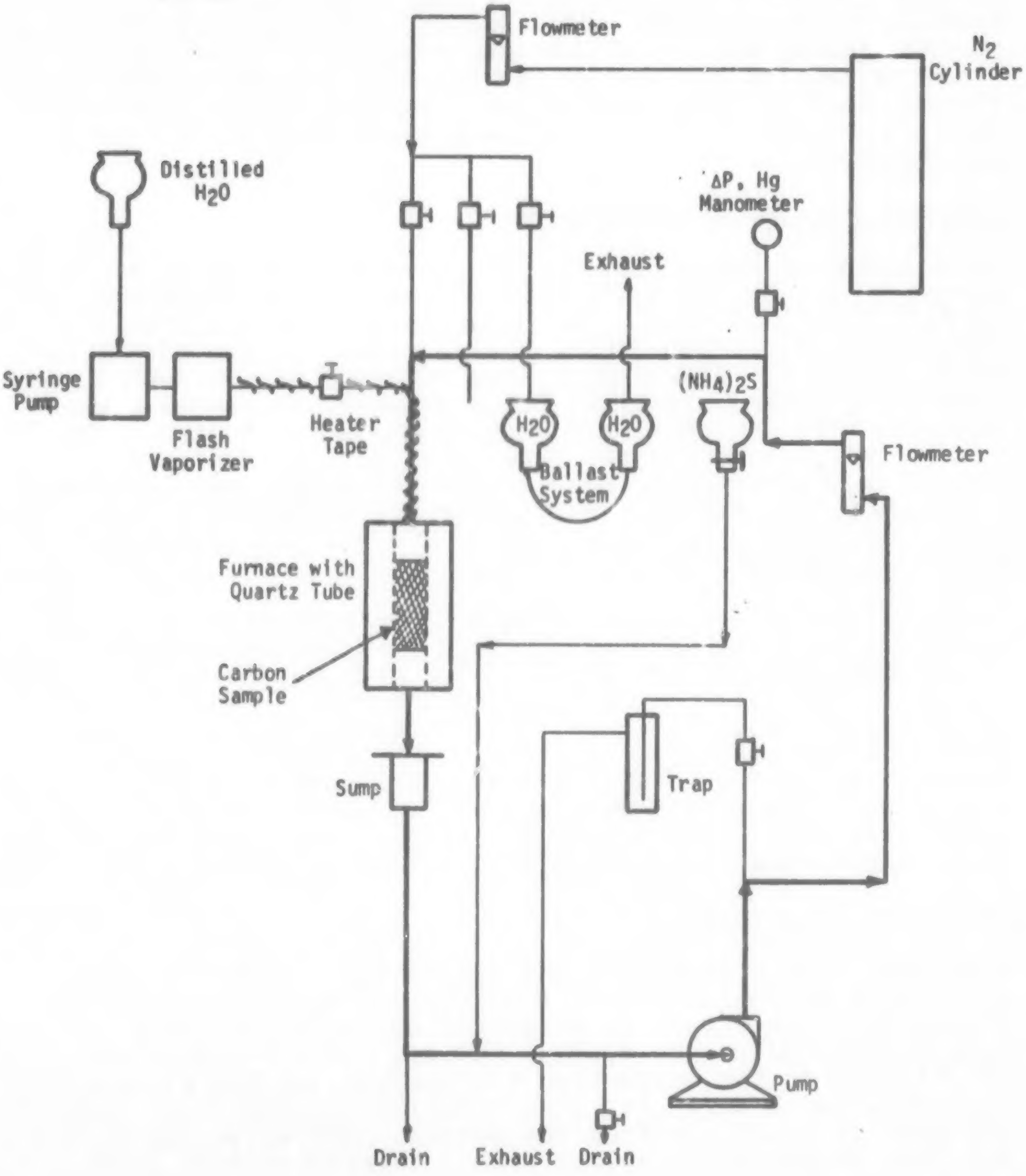
Xylene Extraction -

Twenty grams of a loaded carbon were slurried with 50 ml. of xylene, in a flask with an extended neck and thermometer, at a temperature of 105-110°C (220-230°F) for 20 to 30 minutes. The solvent was decanted and a fresh quantity of solvent added and the procedure repeated. The carbon was sampled between extraction stages. The final carbon was freed of xylene by boiling in water and then oven dried overnight. The xylene extracts after each stage were evaporated on a steam bath and residues oven dried for an hour before weighing to determine sulfur extracted.

Bench Scale Extractor -

A schematic of a recirculating bench scale apparatus used in a study of sulfur extraction from carbon is shown in Figure 25. The carbon to be extracted was placed in a quartz tube inside the Hoskins furnace. The furnace was then heated to the extraction temperature and the system was purged with pure nitrogen or helium metered from a gas cylinder to expel air from the system. The extractant was then added to the system from a separatory funnel and recirculated through the system by a stainless steel centrifugal pump at a rate of 35 ml./min. for 30 minutes.

Figure 25. Flow schematic of recycle extraction apparatus


Flowmeter
N_2 Cylinder
Distilled H_2O
ΔP, Hg Manometer
Exhaust
Syringe Pump
Flash Vaporizer
Heater Tape
H_2O
H_2O
Ballast System
$(NH_4)_2S$
Flowmeter
Furnace with Quartz Tube
Carbon Sample
Sump
Trap
Pump
Drain
Exhaust
Drain

The solvent was then drained from the system, fresh solvent added and the procedure repeated for the desired number of stages. Samples of carbon were taken after each extraction stage, dried and analyzed for sulfur. The extractant was saved for sulfur analysis. After the final extraction the carbon was steamed for eight hours at a known rate by metering water with a syringe pump to a flash vaporizer to produce the steam. The carbon was then cooled under a nitrogen purge, oven dried and analyzed for sulfur. The system contained a water leg for pressure relief, a manometer for pressure measurement and a trap for solvent surges.

5.1.8 Procedures in Bench Scale H_2S Generation Studies

Apparatus for investigating reaction rates of hydrogen and sulfur vapor is shown schematically in Figure 26. Component testing was performed as follows:

1. Sulfur Vapor Generator - The generator, shown in Figure 27, operates by saturation of a stream of nitrogen which is bubbled through molten sulfur. This stream is mixed with the main reaction gas stream and manipulation of the sulfur temperature and the relative flow rates allows adjustment of the final sulfur vapor concentration. Heat is provided by a beaded heater wound on the body of the vessel in such a way as to provide a greater watt density in the upper portions above the liquid level to prevent condensation in this zone. Splashing of the liquid against the higher temperature walls in this zone was to be prevented by an internal baffle. Visual observations through the range of expected operating conditions confirmed that the baffle was operating properly. Tests were also made to determine that the unit could be brought back to room temperature and reheated without difficulties. Maintenance of a low flow of nitrogen during cooling prevents loss of liquid sulfur into the gas dispersion tube which would lead to plugging. It was also found that channeling in the solidifying melt occurs so as to maintain free gas passage through the vessel after cooling, thus allowing inert purging during the next heating cycle.

2. Leak tests showed that the 2" pipe union cap on the sulfur generator would not seal properly under the closing torque which could be applied to the assembled apparatus. Lapping the sealing surfaces allowed tight closure but if another such unit were constructed, the cap should probably be flanged and gasketed.

Figure 26. H2S generation kinetics apparatus

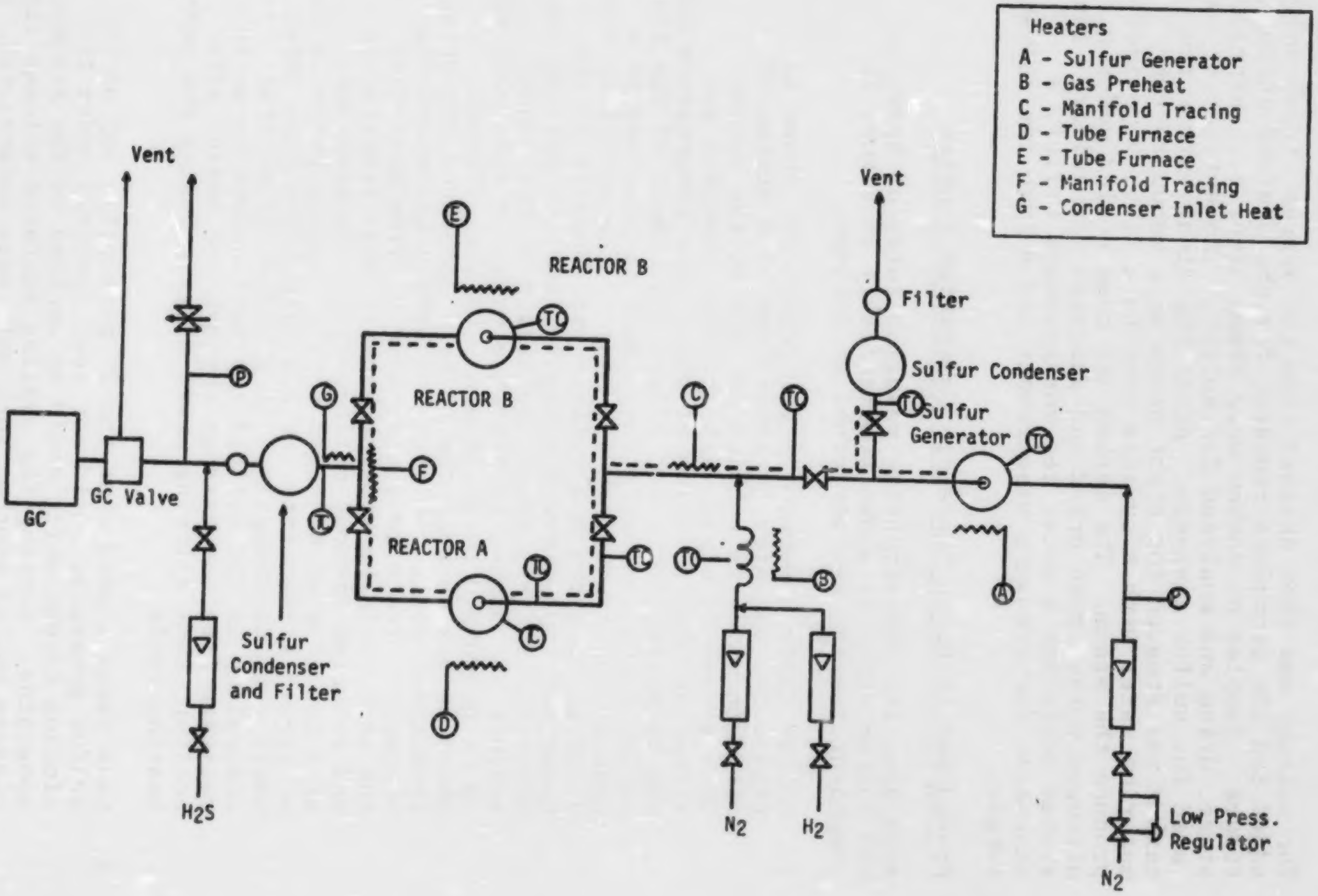
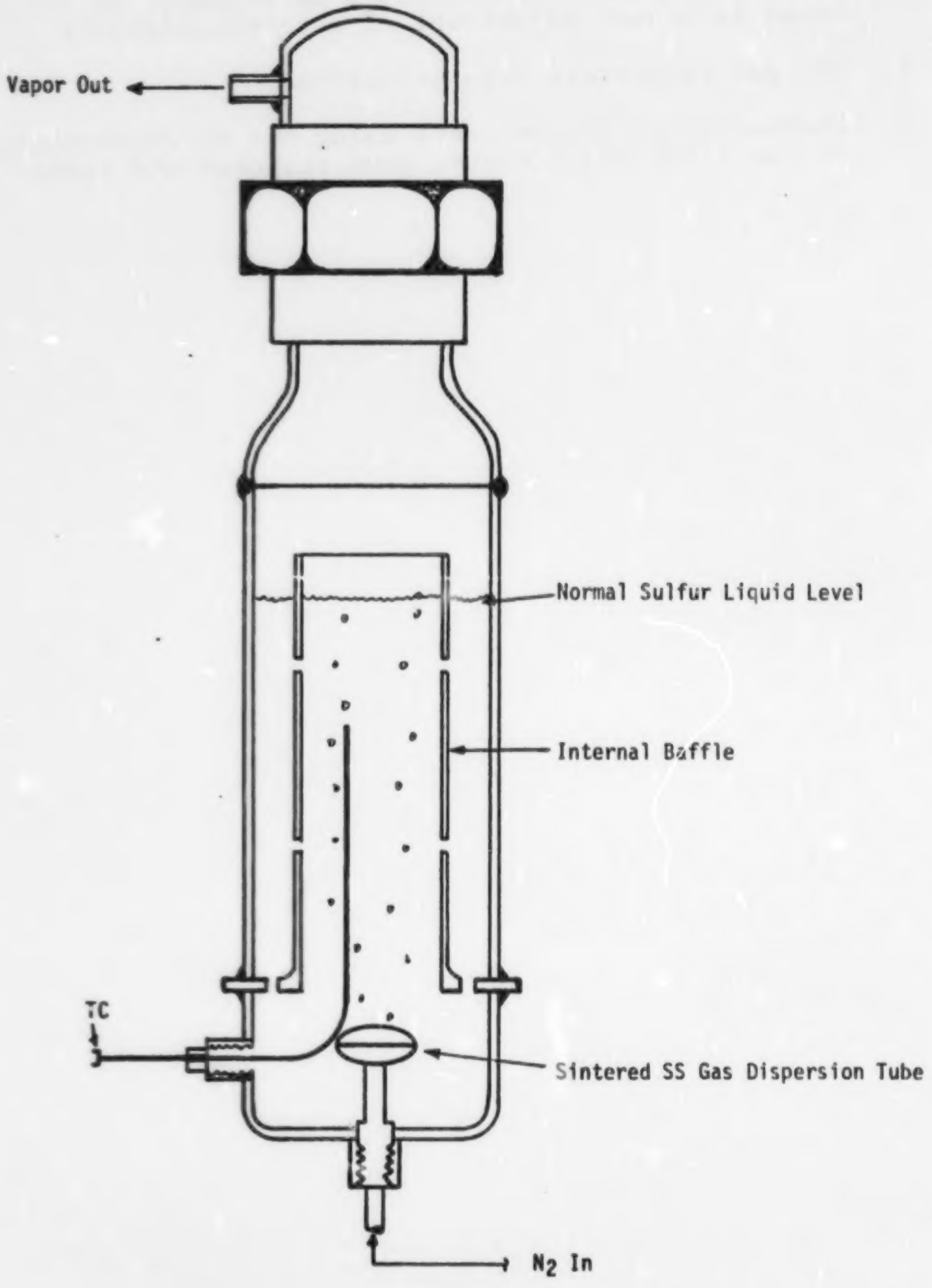

Heaters
A - Sulfur Generator
B - Gas Preheat
C - Manifold Tracing
D - Tube Furnace
E - Tube Furnace
F - Manifold Tracing
G - Condenser Inlet Heat
Vent
Vent
Filter
Sulfur Condenser
Sulfur Generator
TC
P
REACTOR B
REACTOR B
REACTOR A
E
D
F
G
C
B
A
GC
GC Valve
Sulfur Condenser and Filter
H2S
N2
H2
N2
Low Press. Regulator

Figure 27. Sulfur vapor generator


Vapor Out
Normal Sulfur Liquid Level
Internal Baffle
TC
Sintered SS Gas Dispersion Tube
N2 In

3. Heating tests were made to establish power loads required for heatup and maintenance of design temperatures in sevel independent zones. It was found that good temperature control could be obtained in all zones by manual adjustment of auto-transformers.

4. All gas rotameters were calibrated.

5. Chromatograph system tests using H_2S at concentrations in the 1-10% range showed good response and linearity.

5.2 PRE-INTEGRAL RESULTS

5.2.1 SO_2 Sorption

Development of SO_2 Sorption Rate Model -

A large part of the pre-integral SO_2 sorption work was directed toward measurement of the SO_2 kinetics to be used in designing fluid bed adsorbers. A rate model was found to mathematically describe the reaction kinetics and was useful in developing the reactor design procedure. SO_2 sorption is shown in Equation (5):

$$SO_2 + 1/2\ O_2 + H_2O \xrightarrow[\text{Carbon}]{\text{Activated}} H_2SO_4\ \text{(Sorbed)} \tag{5}$$

The reaction rate is defined as the time rate change of acid loading, dX_v/dt,

$$\text{Rate} = \frac{dX_v}{dt} = f(T, X_v, X_S, X_O, y_{SO_2}, y_{O_2}, y_{H_2O}, y_{NO})^* \tag{10}$$

If all variables except acid loading and SO_2 concentration are held constant, the rate equation reduces to the form

$$\frac{dX_v}{dt} = K\ g(X_v)\ h(y_{SO_2}) \tag{11}$$

Several forms of this equation are given in Table 9. These were evaluated by determining how well each could fit the experimental data. The model which best fit the data was then expanded to include the effects of the other important variables.

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*Terms are defined in Section 9, Nomenclature.

Table 9. RATE EXPRESSIONS TO APPROXIMATE SO_2 SORPTION DATA

Designation	Differential Equation
Westvaco	$\frac{dX_v}{dt} = ky_{SO_2}^n(1 - \frac{X_v}{X_{vs}})$
Modified Westvaco	$\frac{dX_v}{dt} = ky_{SO_2}^n(1 - \frac{X_v}{X_{vs}})^2$
Amundson [1]*	$\frac{dX_v}{dt} = ky_{SO_2}(1 - \frac{X_v}{X_{vs}})$
Jost [1]	$\frac{dX_v}{dt} = \frac{y_{SO_2}}{2aX_v + b}$
AVCO [1]	$\frac{dX_v}{dt} = \frac{AX_{vs}Y_{SO_2}}{\left\{1 + \frac{B\left[1 - (1 - \frac{X_v}{X_{vs}})^{1/3}\right]}{(1 - \frac{X_v}{X_{vs}})^{1/3}}\right\}}$
Tracor [1]	$\frac{dX_v}{dt} = ky_{SO_2}(1 - \frac{X_v}{X_{vs}})^n$

The term X_{vs} in Table 9 is the saturation acid loading, for which a value of 0.38 gm. H_2SO_4/gm. carbon was obtained by extrapolation of experimental rate data.

Kinetic data on SO_2 sorption was generated in 21 differential rate experiments in which the weight gain of a carbon sample was monitored as a function of time while the sample was exposed continuously to a constant concentration of SO_2. The apparatus and procedure were described in Section 5.1.1 and the experimental conditions are shown in Table 10.

Raw data in the form of total sample weight versus time was converted to a curve of acid loading versus time. This curve was differentiated by calculating its slope at numerous points to obtain reaction rate values at different acid loadings. The data in this form is included in Appendix A-1 for the 21 differential rate experiments.

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*References listed in Section 8, Bibliography.

Table 10. EXPERIMENTAL CONDITIONS FOR SO_2 SORPTION IN A DIFFERENTIAL RATE APPARATUS

Run Number	Temperature °F	Gas Composition					
		SO_2 PPM	NO PPM	O_2 %	H_2O %	CO_2 %	Inerts %
148, 153	150	2500	150	2	10	11.3	Balance
149	150	1500	150	2	10	11.3	Balance
150	150	500	150	2	10	11.3	Balance
140	200	2500	150	2	10	11.3	Balance
162	200	2000	0	2	10	11.3	Balance
163	200	2000	50	2	10	11.3	Balance
138	200	2000	150	0.7	10	11.3	Balance
160	200	2000	150	2	5	11.3	Balance
139	200	2000	150	2	10	11.3	Balance
157	200	2000	150	2	15	11.3	Balance
144	200	2000	150	3.5	10	11.3	Balance
161	200	2000	300	2	10	11.3	Balance
145	200*	2000	150	2	10	0	Balance
141	200	1500	150	2	10	11.3	Balance
142, 164	200	1000	150	2	10	11.3	Balance
143	200	500	150	2	10	11.3	Balance
151	300	2500	150	2	10	11.3	Balance
152	300	1500	150	2	10	11.3	Balance
158	300	500	150	2	10	11.3	Balance

*N_2 and He were used as the inert gas. Experiments using He versus CO_2 and N_2 showed a small effect on the rate which was within the experimental error.

The initial rate model evaluation was based on Runs 139, 140, 141, 143 and 164. These five runs were conducted at 200°F with all conditions held constant, except for SO_2 concentration, which was varied from 500 to 2500 ppm.

The reaction rate vs. acid loading data given in Appendix A-1 was applied to each rate equation by the following procedure. The Westvaco equation in Table 9, which eventually was selected as the best model, is used as an example. The Westvaco equation

$$\frac{dX_v}{dt} = K\left(1 - \frac{X_v}{X_{vs}}\right) y_{SO_2}^{m} \qquad (12)$$

can be rearranged to the form

$$\ln \left[\frac{dX_v/dt}{1 - X_v/X_{vs}} \right] = \ln K + m \ln y_{SO_2} = Z \qquad (13)$$

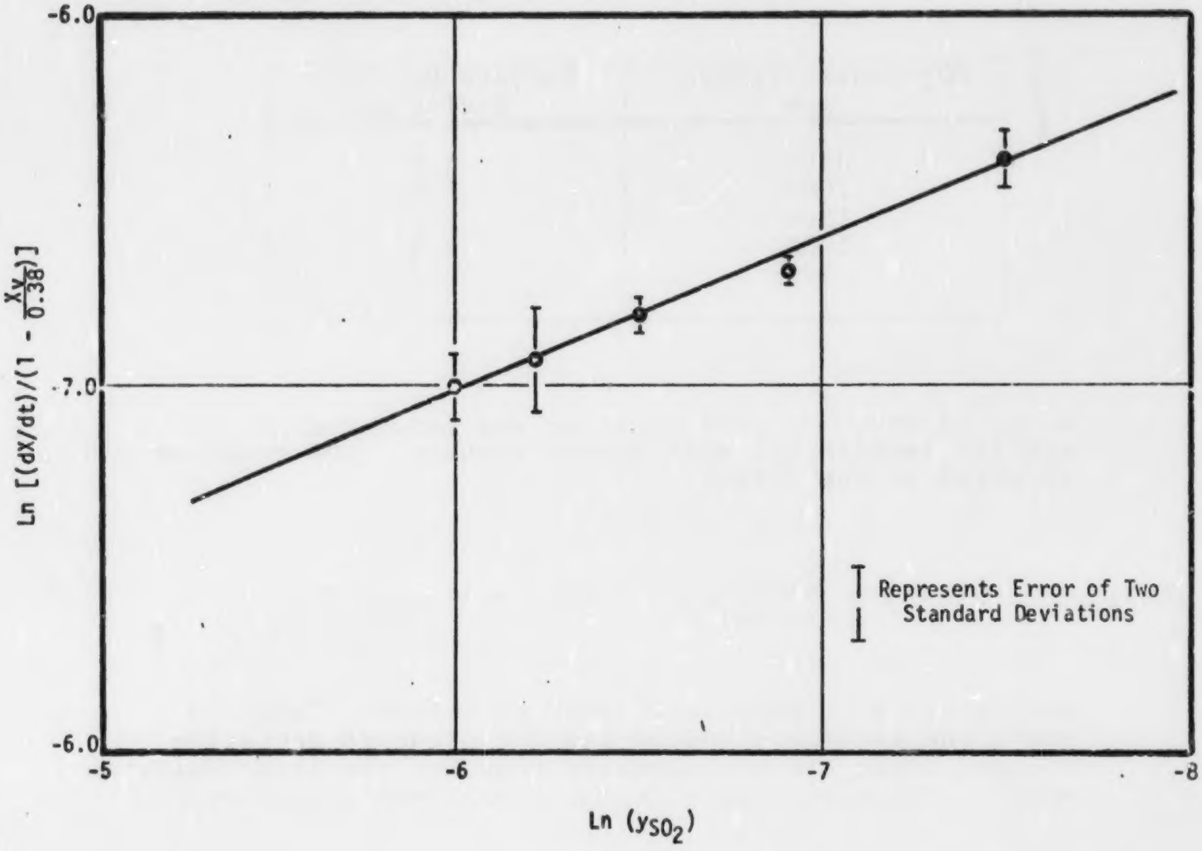
At a constant SO_2 concentration, the right side of the equation is constant, and the values of $\ln \left[\frac{dX_v/dt}{1 - X_v/X_{vs}} \right]$ or Z, calculated from the data, should also be constant if the model is valid. A graph of Z versus $\ln y_{SO_2}$ should give a straight line with a slope of m and an intercept of ln K. Values of Z are tabulated for each run in Appendix A-2. The falues are reasonably constant for acid loadings above 0.01 gm H_2SO_4/gm carbon. The average Z value for each run, omitting data at acid loadings below the 0.01 level, is given in Table 11 with the standard deviation of the data. A plot of Z versus $\ln y_{SO_2}$ is shown in Figure 28. After determination of the constants from the slope and intercept, the resultant rate equation is:

Table 11. STANDARD DEVIATION FOR WESTVACO EQUATION FOR SORPTION DATA AT 200°F WITH NITRIC OXIDE PRESENT FOR ACID LOADING ABOVE 0.01 GM ACID/GM CARBON

Run	SO_2 Conc., ppm	Average z	Standard Deviation
140	2500	-6.99	0.056
139	2000	-7.06	0.069
141	1500	-7.18	0.023
164	1000	-7.30	0.019
143	500	-7.60	0.038

$$\frac{dX_v}{dt} = 0.0105 \left(1 - \frac{X_v}{X_{vs}}\right) y_{SO_2}^{\;0.40} . \qquad (14)$$

Figure 28. Comparison of Westvaco model to sorption data at 200°F



Equation (14) was used to calculate reaction rate values for comparison with the experimental data. The experimental and calculated sets of data are tabulated in Appendix A-3 and the average percent difference between them for each run is given in Table 12. The percentage varies from 1.7 to 6.3% with an overall percent deviation of 4.3%, which is considered very good agreement.

Table 12. DEVIATION OF WESTVACO EQUATION FROM EXPERIMENTAL SO_2 SORPTION RATE DATA AT 200°F WITH NITRIC OXIDE FOR LOADINGS ABOVE 0.01 GM ACID/GM CARBON

SO_2 Concentration, ppm	Average Per Cent Deviation
2500	5.0
2000	6.3
1500	1.7
1000	4.8
500	3.7

A second Westvaco rate equation was evaluated in a similar fashion, but with poorer results. The equation was arranged in the form

(4-7) $$\ln\left[\frac{dX_v/dt}{(1 - X_v/X_{vs})^2}\right] = \ln K + m \ln y_{SO_2} = Z \qquad (15)$$

and values of Z were calculated as before. Table 13 shows the average Z values and the standard deviation values, which are much greater than for the first Westvaco model. The second model clearly does not represent the

Table 13. STANDARD DEVIATION FOR MODIFIED WESTVACO EQUATION FOR SORPTION DATA AT 200°F WITH NITRIC OXIDE FOR ACID LOADING ABOVE 0.01 GM ACID/GM CARBON

SO2 Concentration, ppm	Average z	Standard Deviation
2500	-6.77	0.200
2000	-6.82	0.238
1500	-6.94	0.176
1000	-7.09	0.161
500	-7.39	0.162

experimental data as well as the first model does. The other models were also evaluated by similar techniques, but none represented the data as well as the first Westvaco model. The evaluation of these other models is included in Appendix J-1.

After selecting the Westvaco model as the basic form of the rate expression and determining the order of the reaction with respect to SO_2 concentration, further experiments were conducted in order to expand the equation to include effects of O_2, H_2O, and NO concentrations and of temperature. The simplifying assumption was made that there is no first order interaction of variables. This allowed a stepwise determination of each variable's effect.

For example, to determine the dependency on O_2 concentration, Equation (14) was modified to yield

$$\frac{dX_v}{dt} = K\, y_{SO_2}^{0.40}\, y_{O_2}^{n}\, \left(1 - \frac{X_v}{X_{vs}}\right) \qquad (16)$$

which reduces to Equation (14) if $K\, y_{O_2}^{n} = 0.0105$. If Equation (16) is arranged in the form

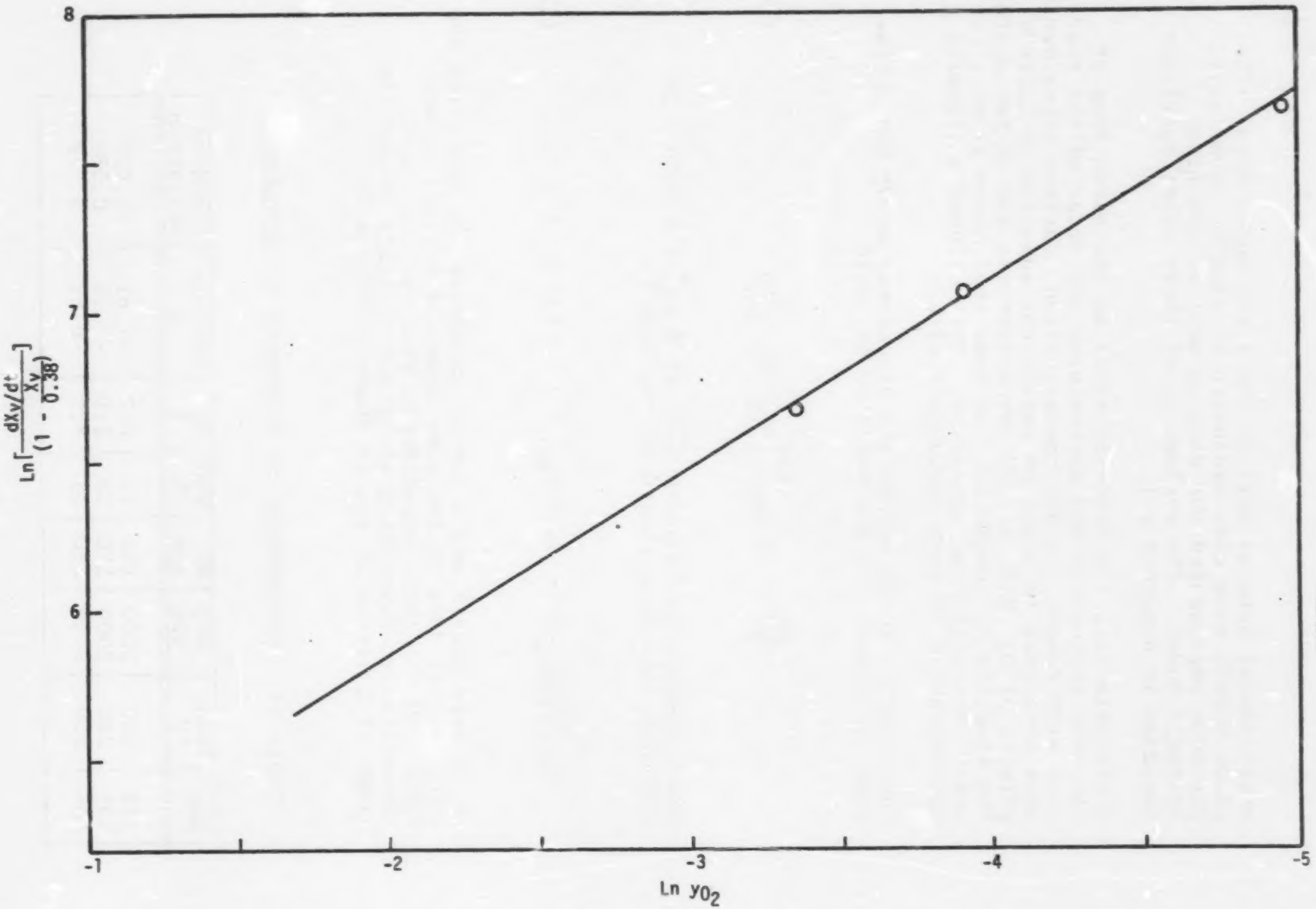
$$\ln\left[\frac{dX_v/dt}{1 - X_v/X_{vs}}\right] = \ln\left[K\, y_{SO_2}^{0.40}\right] + n\left[\ln y_{O_2}\right] = Z \qquad (17)$$

it is seen that K and n can be determined by analyzing the experimental data in the same manner described before. Data from the three experiments used to find the O_2 concentration dependency are given in Table 14 and the graph of Z versus $\ln y_{O_2}$ is shown in Figure 29.

Table 14. EXPERIMENTS TO DETERMINE O_2 DEPENDENCY

Run	Temp. °F	SO_2 ppm	NO ppm	H_2O %	O_2 %	Average Z	Standard Deviation
138	200	2000	150	10	0.7	-7.67	0.053
139	200	2000	150	10	2.0	-7.06	0.080
144	200	2000	150	10	3.7	-6.67	0.072

Figure 29. Effect of O_2 on SO_2 sorption at 200°F with NO present



The values of K and n are obtained graphically, and the order of the reaction with respect to oxygen is found to be 0.63. The new K value is 0.1245 so that the rate equation now becomes

$$\frac{dX_v}{dt} = 0.1245\, y_{SO_2}^{0.40}\, y_{O_2}^{0.63} \left(1 - \frac{X_v}{X_{vs}}\right) \quad \text{for} \left[\begin{array}{l} T = 200°F \\ NO = 150 \text{ ppm} \\ H_2O = 10\% \end{array}\right. \tag{18}$$

The H_2O dependency is found in the same manner. Data from the pertinent experiments is given in Table 15, and the graph of Z versus $\ln y_{SO_2}$ is shown in Figure 30.

Table 15. EXPERIMENTS TO DETERMINE H_2O DEPENDENCY

Run	Temp. °F	SO_2 ppm	NO ppm	O_2 %	H_2O %	Average Z	Standard Deviation
160	200	2000	150	2	5	-7.56	0.164
139	200	2000	150	2	10	-7.06	0.080
144	200	2000	150	2	15	-6.76	0.031

The graph is a straight line, and the order of the reaction with respect to H_2O is 0.73. The new K is 0.667 and the rate equation becomes

$$\frac{dX_v}{dt} = 0.667\, y_{SO_2}^{0.40}\, y_{O_2}^{0.63}\, y_{H_2O}^{0.73} \left(1 - \frac{X_v}{X_{vs}}\right) \quad \text{for} \left[\begin{array}{l} T = 200°F \\ NO = 150 \text{ ppm} \end{array}\right. \tag{19}$$

The NO dependency was treated in a similar manner, but in this case the results showed a zero order dependency at NO concentrations above 100 ppm. The data is presented in Table 16 and Figure 31.

Table 16. EXPERIMENTS TO DETERMINE NITRIC OXIDE DEPENDENCY

Run	Temp. °F	SO_2 ppm	O_2 %	H_2O %	NO ppm	Average Z	Standard Deviation
162	200	2000	2	10	0	-5.97	0.214
163	200	2000	2	10	50	-6.88	0.048
139	200	2000	2	10	150	-7.06	0.080
161	200	2000	2	10	300	-7.07	0.086

Figure 30. Effect of H_2O concentration on SO_2 sorption at 200°F with NO present

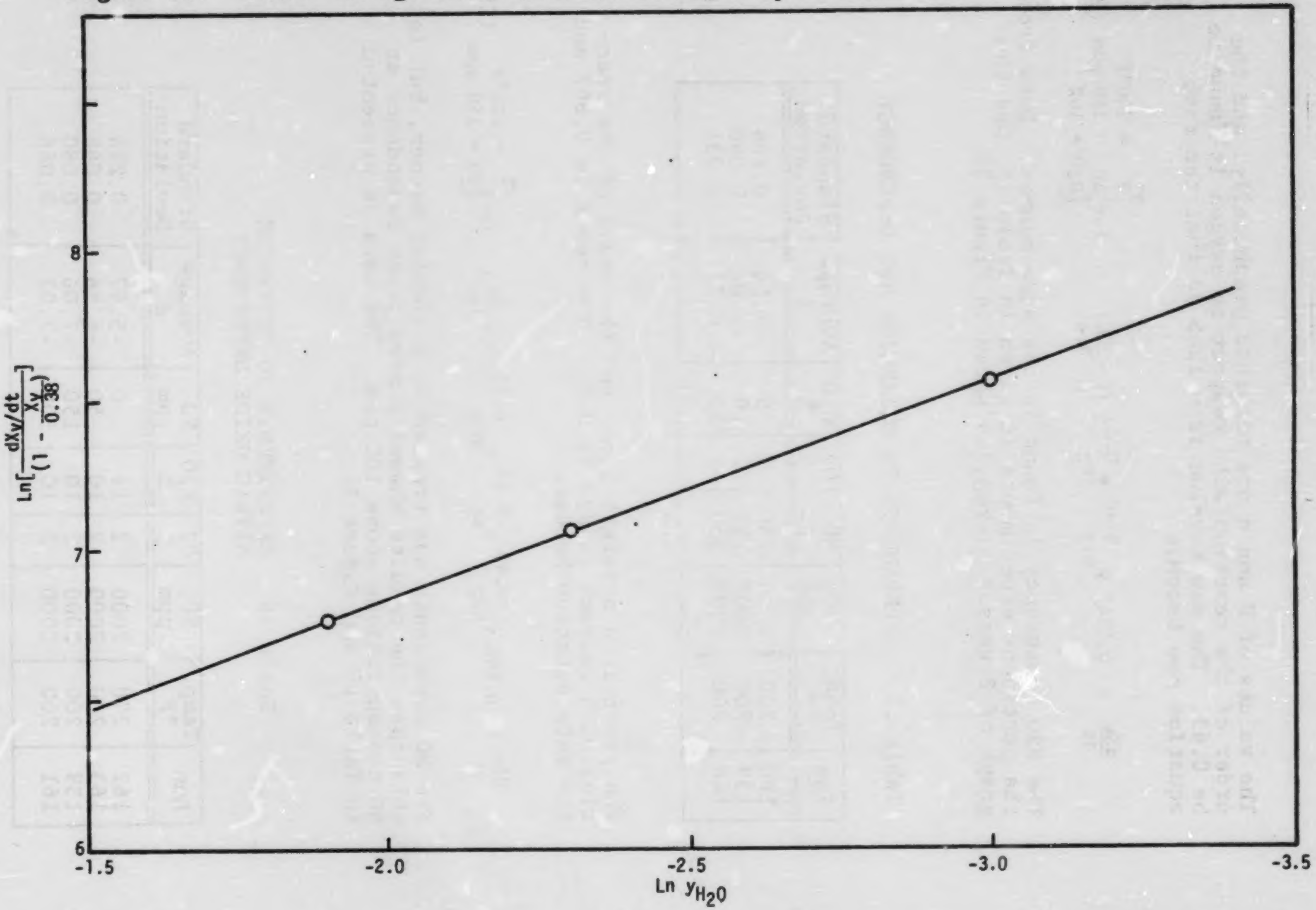
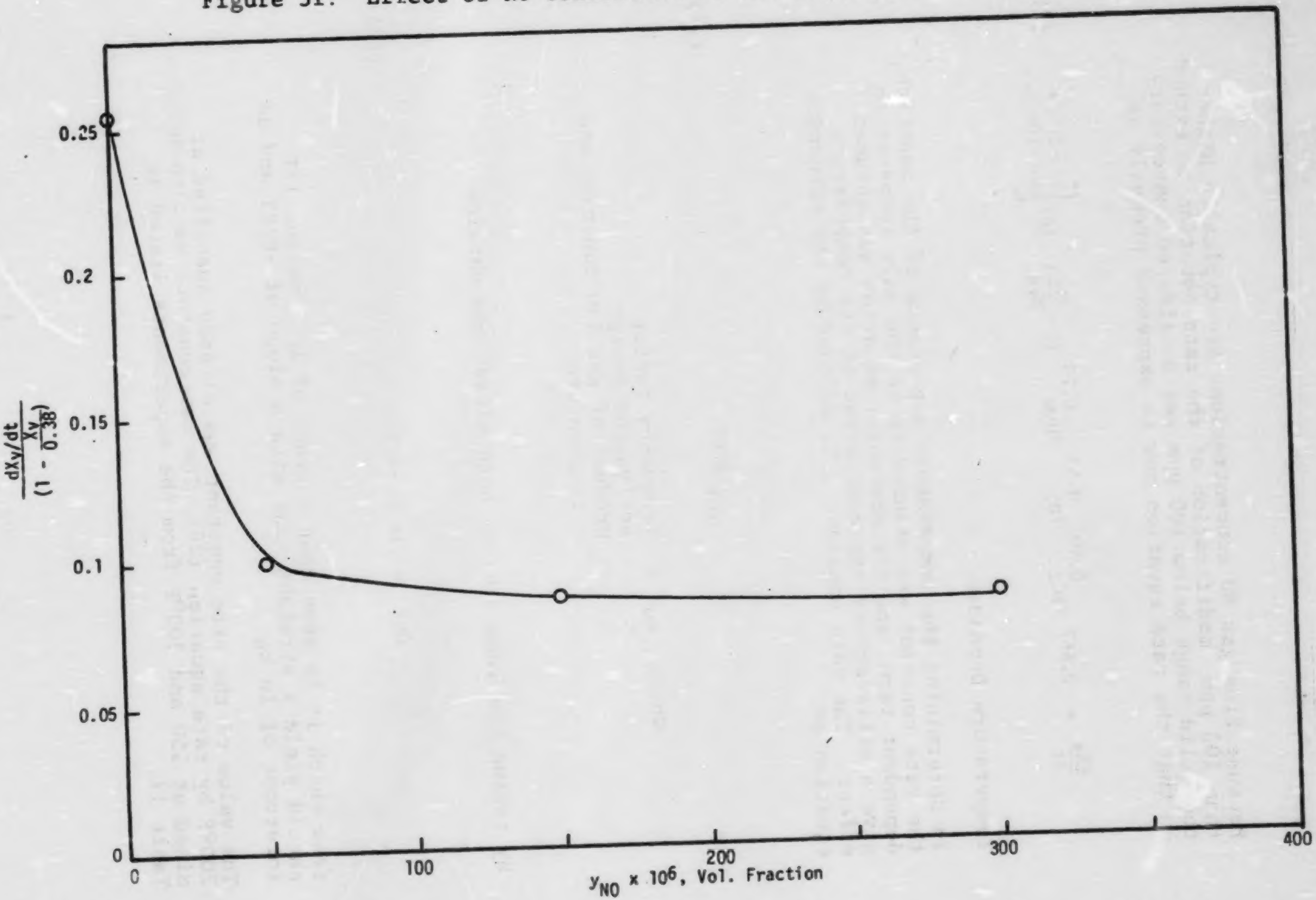


Figure 31. Effect of NO concentration on SO_2 sorption at 200°F



Because flue gas NO concentrations are typically higher than 100 ppm, modification of the rate equation to extend the valid range below 100 ppm was considered unnecessary, so that the rate equation now is expressed properly as

$$\frac{dX_v}{dt} = 0.667\, y_{SO_2}^{0.40}\, y_{O_2}^{0.63}\, y_{H_2O}^{0.73} \left(1 - \frac{X_v}{X_{vs}}\right) \quad \text{for} \left[\begin{array}{l} T = 200°F \\ NO > 100 \text{ ppm} \end{array}\right. \qquad (20)$$

Temperature Dependence -

In determining the temperature dependence of the reaction, the rate constant was assumed to be the only temperature dependent term, and the Arrhenius equation was assumed to give a satisfactory representation of the temperature effect. The rate constant K is defined by the Arrhenius equation as

$$K = k_o\, e^{-E/RT} \qquad (21)$$

where k_o = frequency factor
E = activation energy
RT = product of gas law constant and temperature.

By taking the logarithm of both sides, one obtains

$$\ln K = \ln k_o - E/RT \qquad (22)$$

from which it is seen that a graph of ln k versus 1/T should yield a straight line with a slope of -E/RT and an intercept of ln k_o.

The value of the rate constant was already specified at 200°F by rate equation (20). The rate constant was also determined at 150 and 300°F from the experiments listed in Table 17.

Table 17. EXPERIMENTS TO DETERMINE THE EFFECT OF TEMPERATURE ON SO_2 SORPTION

Run	Temperature °F	Gas Composition				Average Z	Standard Deviation
		SO_2 ppm	NO ppm	O_2 %	H_2O %		
148-G	150	2500	150	2	10	-6.01	0.688
153-G	150	2500	150	2	10	-6.25	0.569
149-G	150	1500	150	2	10	-6.22	0.659
150-G	150	500	150	2	10	-6.76	0.469
140-G	200	2500	150	2	10	-6.99	0.056
139-G	200	2000	150	2	10	-7.06	0.080
141-G	200	1500	150	2	10	-7.18	0.025
142-G	200	1000	150	2	10	-7.39	0.086
164-G	200	1000	150	2	10	-7.30	0.019
143-G	200	500	150	2	10	-7.60	0.038
151-G	300	2500	150	2	10	-7.49	0.149
152-G	300	1500	150	2	10	-8.08	0.211
158-G	300	500	150	2	10	-8.76	0.323

Values of Z and the standard deviation of the data are also included in the table. To calculate the rate constants at 150 and 300°F, the Z values were plotted versus ln y_{SO_2} as seen in Figure 32. Straight lines were drawn through the points subject to the constraint that the order of the reaction with respect to SO_2 was not a function of temperature so that the slope was constant. Once the lines were drawn, the rate constants could be found by inserting the Z and ln y_{SO_2} coordinates of any point on a line into equation

$$Z = \ln K \, y_{O_2}^{0.63} \, y_{H_2O}^{0.73} + 0.40 \ln y_{SO_2} \qquad (23)$$

and then solving for k. Table 18 gives the rate constants at three different temperatures. Figure 33 is

Table 18. RATE CONSTANTS FOR THE WESTVACO MODEL

Temperature, °F	Rate Constant, gm acid/gms carbon/min.
150	1.476
200	0.667
300	0.244

Figure 32. Effect of temperature on the Westvaco model with constant order of reaction for SO_2

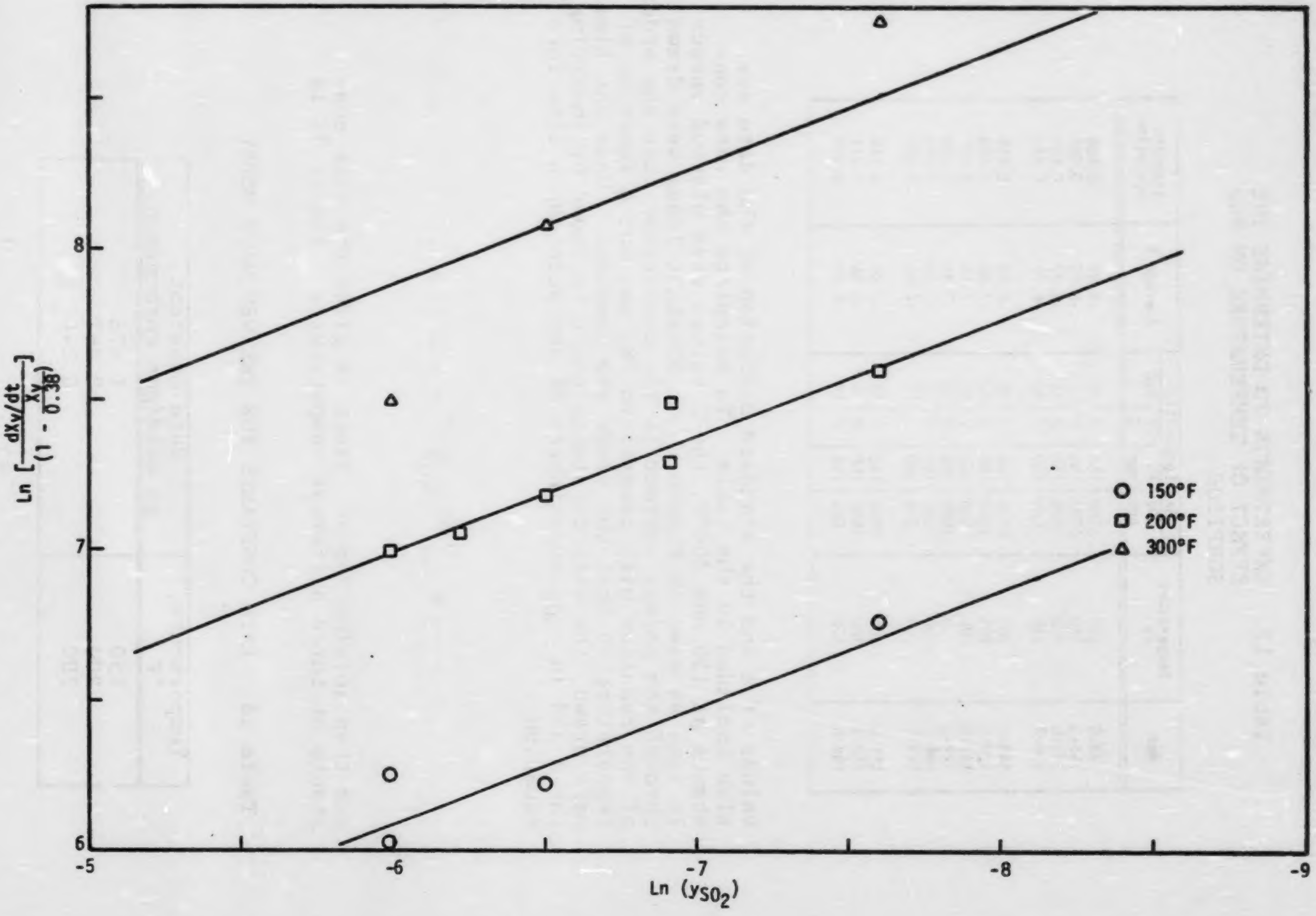
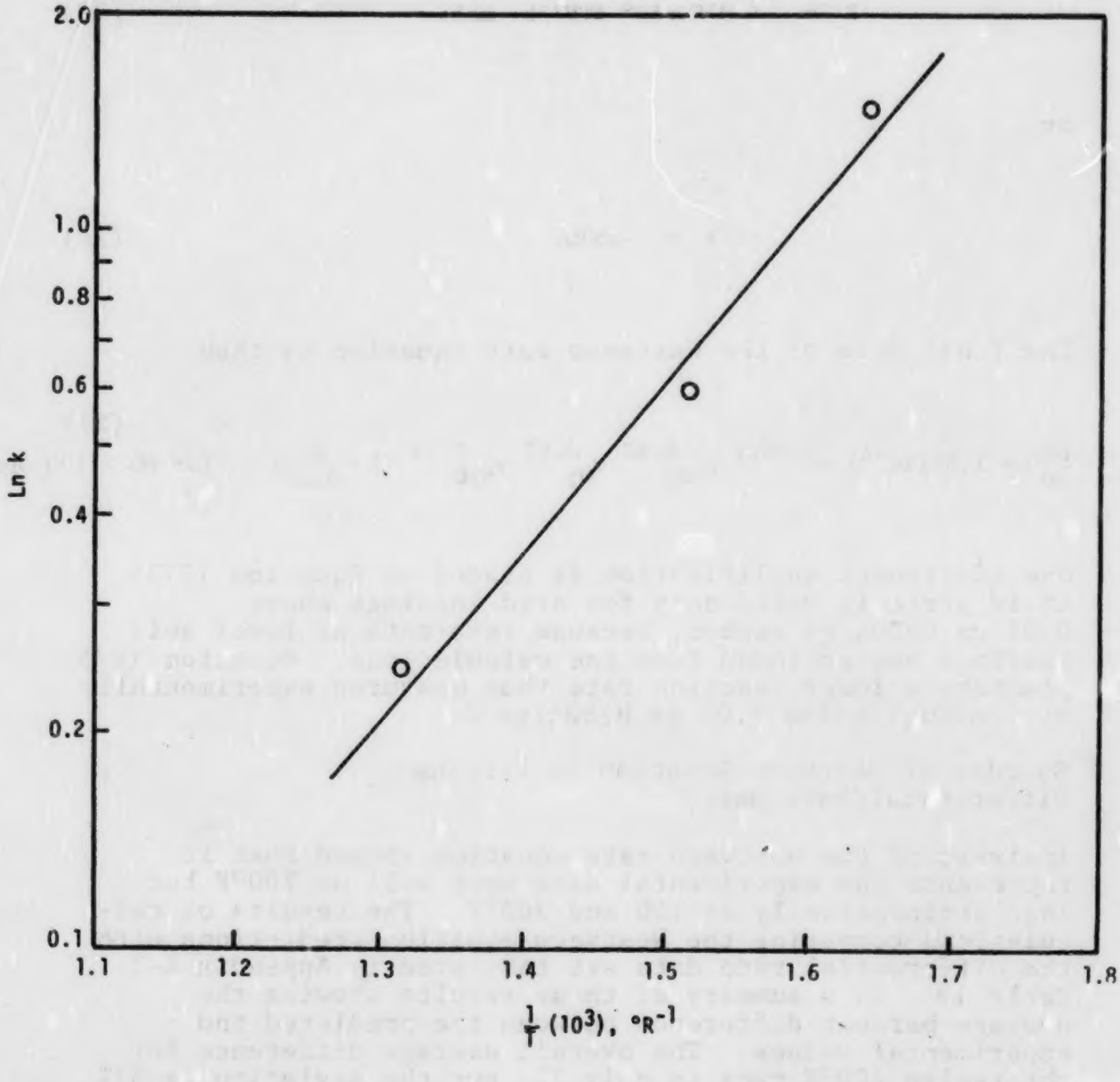


Figure 33. Rate constant as a function of temperature for SO_2 sorption



the graph of ln K versus 1/T from which the frequency factor and the activation energy were obtained. The results are

$$k_o = 1.59 \times 10^{-4} \tag{24}$$

$$E = -1.079 \times 10^{4} \text{ BTU/lb. mole} \tag{25}$$

or

$$E/R = -5520. \tag{26}$$

The final form of the Westvaco rate equation is then

$$\frac{dX_v}{dt} = 1.59(10^{-4})\, e^{5520/T}\, y_{SO_2}^{0.40}\, y_{O_2}^{0.63}\, y_{H_2O}^{0.73}\, \left(1 - \frac{X_v}{0.38}\right) \quad \text{for NO > 100 ppm} \tag{27}$$

One additional qualification is placed on Equation (27); it is strictly valid only for acid loadings above 0.01 gm H_2SO_4/gm carbon, because rate data at lower acid loadings was excluded from the calculations. Equation (27) predicts a lower reaction rate than measured experimentally at loadings below 0.01 gm H_2SO_4/gm C.

Success of Westvaco Equation in Fitting Differential Rate Data

Analysis of the Westvaco rate equation showed that it represents the experimental data very well at 200°F but less satisfactorily at 150 and 300°F. The results of calculations comparing the Westvaco equation predictions with the differential rate data are tabulated in Appendix A-3. Table 19 is a summary of these results showing the average percent difference between the predicted and experimental values. The overall average difference for the twelve 200°F runs is only 7%, but the deviation is 37% at 150°F and 23% at 300°F.

Table 19. DEVIATION OF WESTVACO MODEL FROM DIFFERENTIAL RATE DATA FOR ACID LOADINGS ABOVE 0.01 GM ACID/ GM CARBON

Run	Temperature °F	Average % Deviation
138	200	4.5
139	"	7.7
140	"	8.1
141	"	5.6
142	"	1.9
143	"	3.9
144	"	6.6
145	"	5.0
157	"	4.8
160	"	13.9
161	"	8.0
164	"	12.3
AVERAGE	200	6.9
148	150	47.7
149	"	40.0
150	"	20.6
153	"	39.2
AVERAGE	150	36.9
151	300	36.8
152	"	15.9
158	"	17.4
AVERAGE	300	23.4

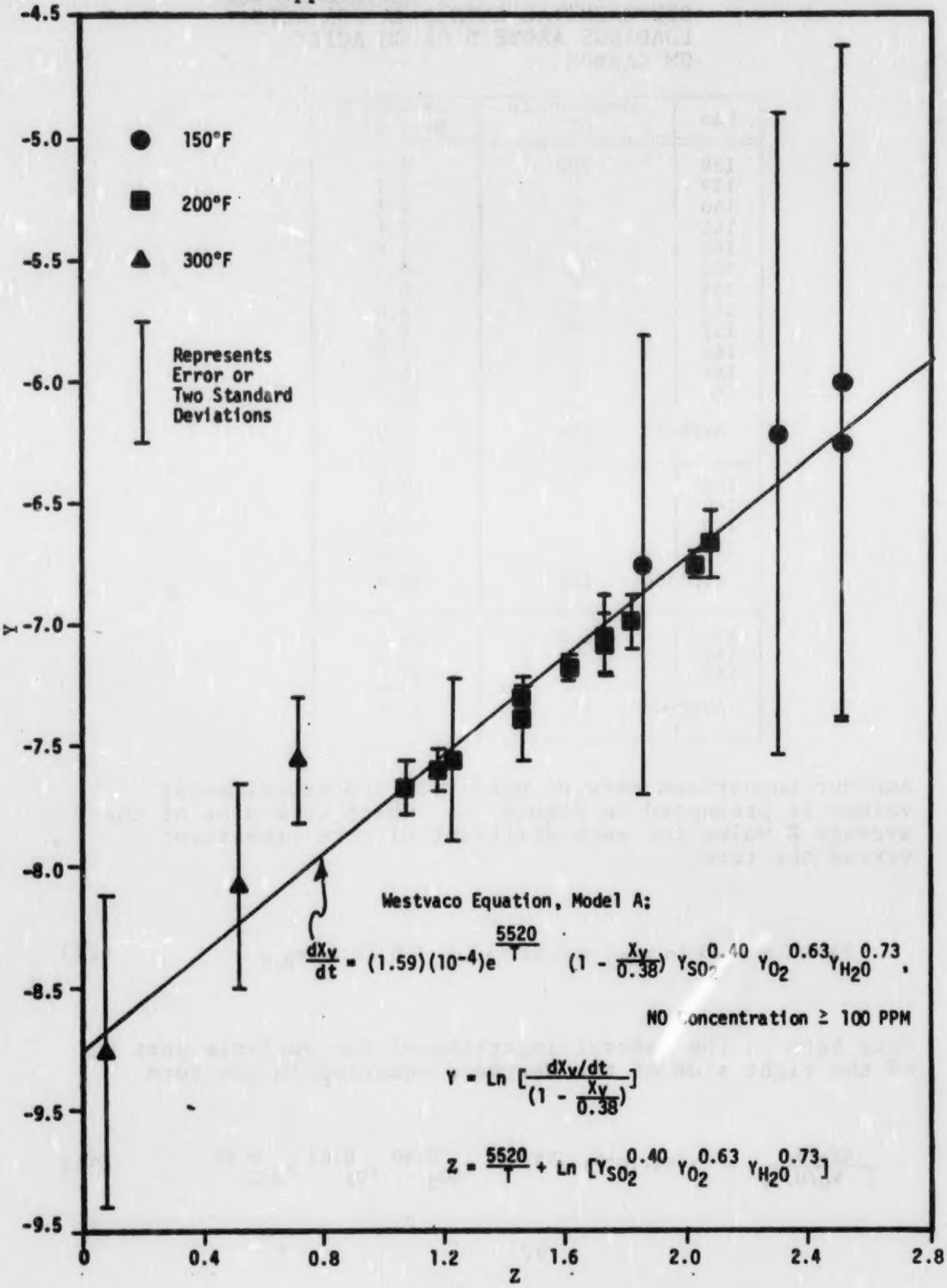
Another comparison between predicted and experimental values is presented in Figure 34, which is a plot of the average Z value for each differential rate experiment versus the term

$$5520/T + 0.40 \ln y_{SO_2} + 0.63 \ln y_{O_2} + 0.73 \ln y_{H_2O} \qquad (28)$$

This term is the natural logarithm of the variable part of the right side of the Westvaco equation in the form

$$\frac{dX_v/dt}{1 - X_v/0.38} = 1.59(10^{-4})\, e^{5520/T}\, y_{SO_2}^{\;0.40}\, y_{O_2}^{\;0.63}\, y_{H_2O}^{\;0.73} \qquad (29)$$

Figure 34. Comparison of the Westvaco Model A to experimental SO_2 sorption on activated carbon in differential rate apparatus



The straight line in Figure 34 represents the Westvaco equation as the natural log of both sides of the above expression. The experimental Z values are shown with an error band representing twice the standard deviation of the data. The Z values and standard deviations are in Table 17.

The standard deviation provides a useful measure of the data's probable accuracy. There is a 95% probability that the true Z value lies within an error band that is two standard deviations wide, so that a small standard deviation indicates high accuracy of the data. It is seen from Table 17 and Figure 34 that the standard deviation of the data is much smaller at 200°F than at 150 or 300°F. As a percentage of the average Z value, the standard deviation averages 0.7% at 200°F, 2.8% at 300°F, and 9.4% at 150°F, so that statistically, the 200°F data is excellent but the 150 and 300°F data is not as good.

Sorber Design Study - Effects on Size -

Based on the Westvaco SO_2 sorption rate expression and two important reactor model assumptions, a procedure was developed for calculating the required size of a multistage fluid bed SO_2 sorption reactor. Using this procedure a sorber design study was made encompassing the effects of seven important variables. The complete derivation of the design equations is in Appendix C.

The two important reactor model assumptions concerned the flow characteristics of the gas and carbon phases within the reactor. It was assumed that the carbon phase was well-mixed on each stage, so that the carbon beds represented a series of backmix reactors. Plug flow was assumed for the gas phase.

The design equations used in the reactor size calculation procedure are:

$$(Y_{SO_2})_{j+1}^{0.6} = (Y_{SO_2})_j^{0.6} - 3.687(10^{-4}) \left[\frac{(1 - \frac{XV_j}{0.38})\, Y_{O_2}^{0.63}\, Y_{H_2O}^{0.73}\, hD^2\, e^{5520/T}}{q_T} \right] \quad (30)$$

$$XV_{j+1} = XV_j - (\frac{q_T}{386})(\frac{98}{R_c}) \left[(Y_{SO_2})_j - (Y_{SO_2})_{j+1} \right] \quad (31)$$

The first equation (30) was the acid loading and SO_2 concentration on a given stage to calculate the SO_2 concentration on the next stage. The second equation (31) is a material balance relationship which is used to calculate the acid loading on the new stage from the other variables. Using these equations, plate-to-plate calculations are made beginning with the bottom stage of the reactor and proceeding until the end conditions at the top of the reactor are reached. This determines the required number of stages and hence the reactor size.

A computer program was written to facilitate the calculational procedure. A listing of the program is an Appendix E. The effects of the following parameters on reactor size were studied:

1) Inlet SO_2 concentration (2,000 ppm)
2) Inlet O_2 concentration (0.046 mole fraction)
3) Inlet H_2O concentration (0.13 mole fraction)
4) Outlet acid loading on carbon (0.184 lb. acid/ lb. carbon)
5) Temperature (200°F)
6) Linear Gas Velocity (4 ft./sec.)
7) Carbon bed depth/stage (9 inches).

Each parameter was varied separately while holding all others constant at the base conditions given in parentheses in the preceding list. The results of the design study are in Appendix A-9.

Attempts To Further Improve Model by Multiple Regression Analyses

Multiple regression analyses were carried out in an attempt to improve the Westvaco model's representation of the data at 150 and 300°F. Based on the following form of the rate equation,

$$\frac{dX_v}{dt} = k\, e^{-E/RT}\, y_{SO_2}^{\,m}\, y_{O_2}^{\,p}\, y_{H_2O}^{\,q} \left(1 - \frac{X_v}{0.38}\right)^{A} \qquad (32)$$

The multiple regression analyses were used to determine the best values of the constants k, E/R, m, p, and q for the two cases where the order of reaction relative to the acid concentration in the carbon phase, constant A, was allowed to vary in one case and equal to 1.0 in the other case. Both cases were processed by computer using a program written by IBM. A listing of the program is in Appendix E-1. The Westvaco equation, (27), was designated Model A, and the multiple regression variations were designated Models B and C. For Model B with A = 1.0 the multiple regression analysis yielded the following expression:

$$\frac{dX_v}{dt} = 3.32(10^{-4})\, e^{5416/T}\, {y_{SO_2}}^{0.53}\, {y_{O_2}}^{0.62}\, {y_{H_2O}}^{0.73}\, \left(1 - \frac{X_v}{0.38}\right) \qquad (33)$$

Allowing the constant A to seek its statistical value resulted in the following expression for Model C:

$$\frac{dX_v}{dt} = 3.42(10^{-4})\, e^{5732/T}\, {y_{SO_2}}^{0.53}\, {y_{O_2}}^{0.62}\, {y_{H_2O}}^{0.73}\, \left(1 - \frac{X_v}{0.38}\right)^{1.83} \qquad (34)$$

Calculations were carried out on the computer to compare Models B and C with the differential rate data and the results are included in Appendix A-7. Table 20 is a summary of these results showing the average percent difference between the predicted and experimental values.

Figures 34, 35, and 36 provide a graphical comparison of the three models. The results in Table 20 show that Model B fits the data slightly better than Model A at 300°F but not as well at 150°F, while Model C provides a significant improvement at both 150 and 300°F. At 200°F Models B and C are both worse than Model A, as expected. Clearly, Model B does not offer any real improvement at 150°F to warrant its substitution for Model A near this temperature and perhaps over the 150 to 175°F range, but Model A remains the best choice over the remainder of the temperature range from 175 to 300°F, because of its superior performance at 200°F.

Table 20. DEVIATION OF MULTIPLE REGRESSION MODELS FROM DIFFERENTIAL RATE DATA FOR ACID LOADINGS ABOVE 0.01 GM ACID/GM CARBON

Run	Temperature °F	Average Percent Deviation		
		Model A	Model B	Model C
138	200	4.5	13.6	22.8
139	"	7.7	17.6	25.9
140	"	8.1	23.1	30.7
141	"	5.6	16.3	19.5
142	"	1.9	8.1	13.9
143	"	3.9	4.6	11.1
144	"	6.6	13.1	24.5
145	"	5.0	8.0	14.6
157	"	4.8	18.1	21.3
160	"	13.9	24.1	26.8
161	"	8.0	20.5	24.5
164	"	12.3	18.4	26.1
AVERAGE	200	6.9	15.5	21.8
148	150	47.7	51.3	33.5
149	"	40.0	41.0	25.8
150	"	20.6	20.7	13.2
153	"	39.2	47.6	22.1
AVERAGE	150	36.9	40.2	23.6
151	300	36.8	25.9	27.6
152	"	15.9	16.1	8.2
158	"	17.4	19.4	5.0
AVERAGE	300	23.4	20.5	13.6

Figure 35. Comparison of the Westvaco Model B to experimental SO_2 sorption on activated carbon in differential rate apparatus

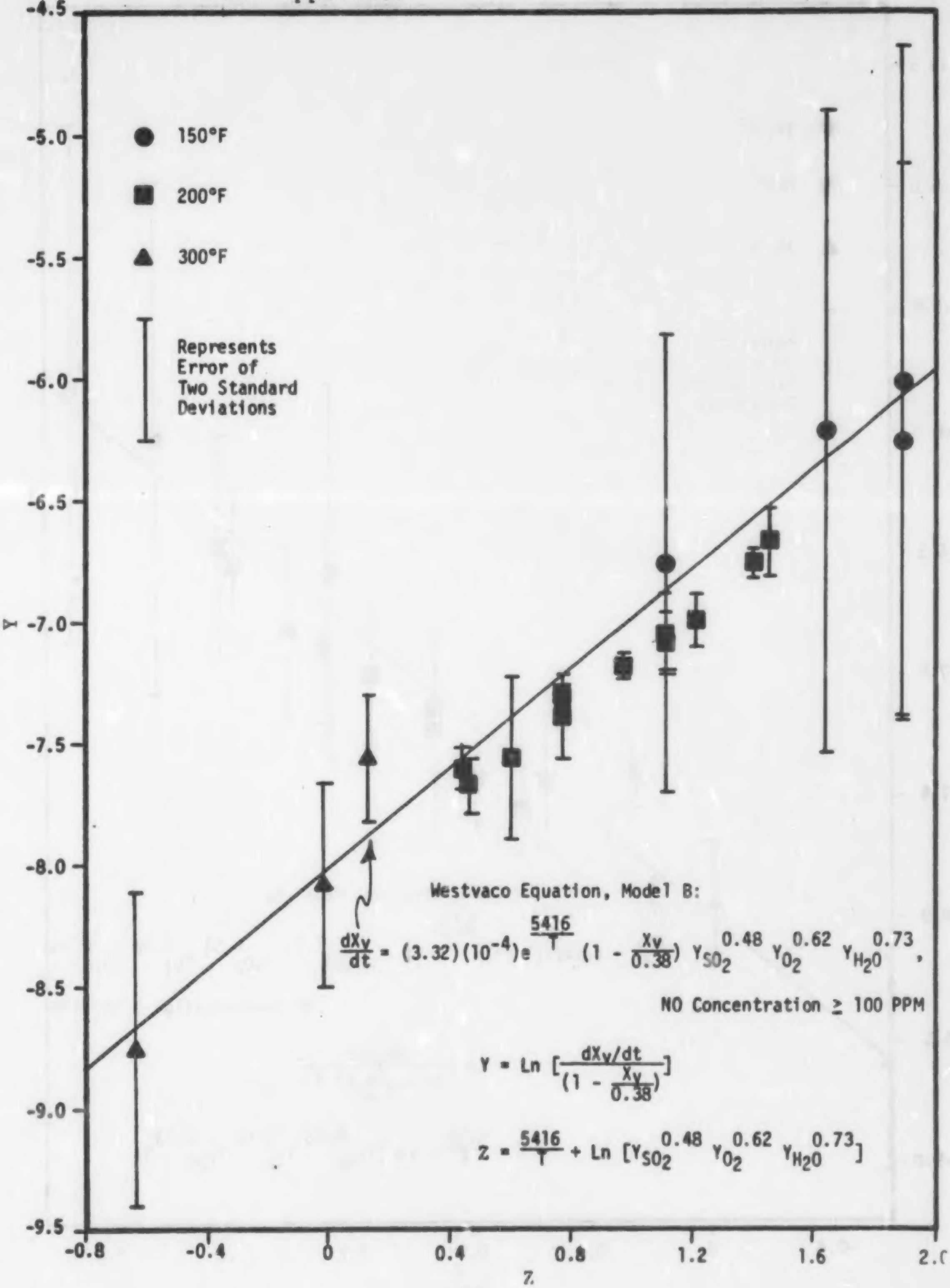
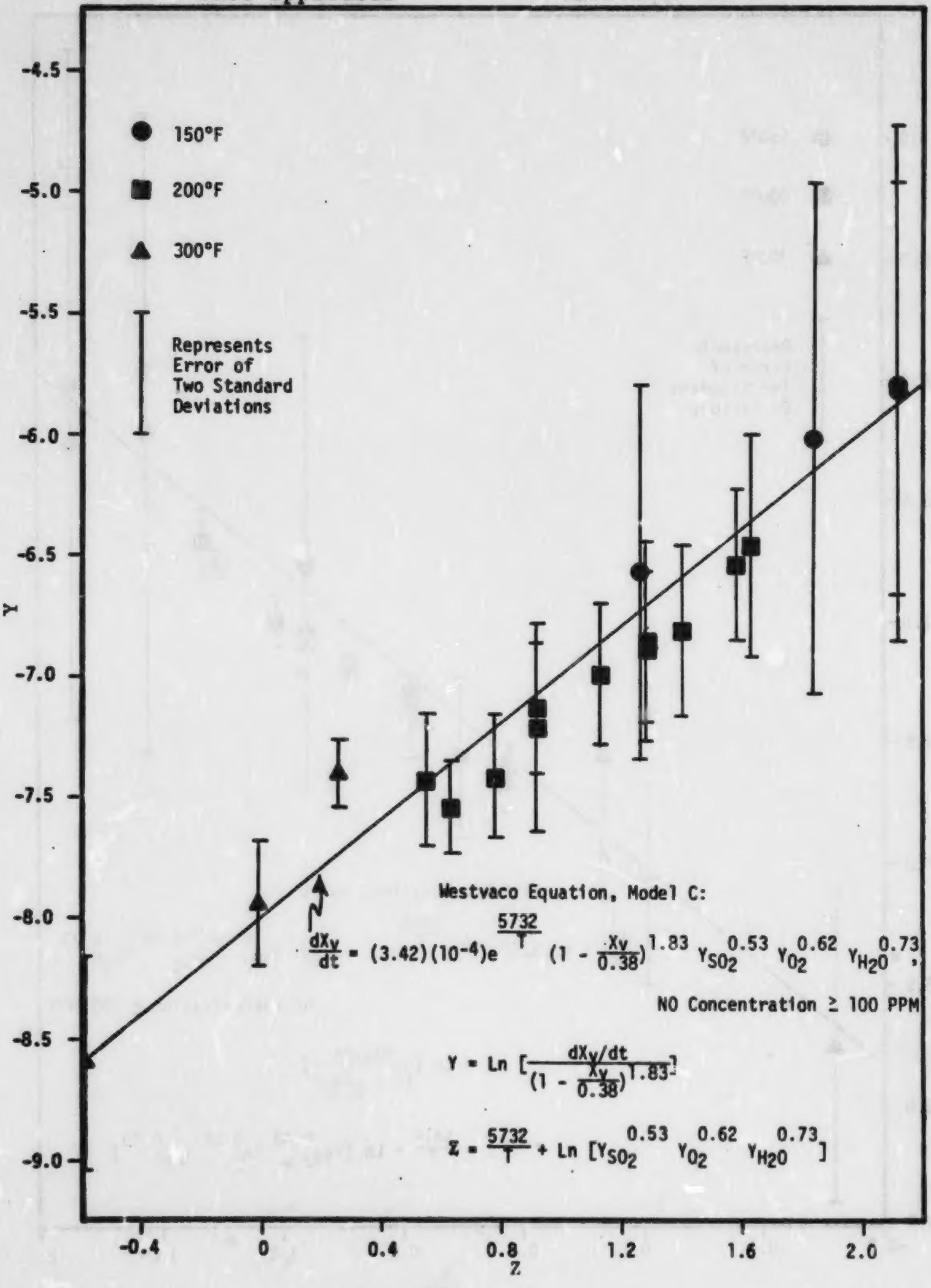


Figure 36. Comparison of the Westvaco Model C to experimental SO_2 sorption on activated carbon in differential rate apparatus



In the Westvaco equation (Model A) the rate is proportional to $(1 - X_V/0.38)$ or equivalently, to $(0.38 - X_V)$ where $0 < X_V < 0.38$. This model is valid if the plot of dX_V/dt versus X_V is a straight line. Examination of the rate curves in Figure 28 reveals that dX_V/dt versus X_V approaches a straight line at both 200 and 300°F, but not at 150°F. Model A should, therefore, give satisfactory results at the higher temperatures, but a different model may necessarily be needed at 150°F. In Model C the rate is proportional to $(1 - X_V/0.38)^{1.83}$ which provides a better fit at 150°F.

From Figure 37 it is seen that the 200 and 300°F curves are not linear until the acid loading is above 1 gm/100 gms carbon. This explains why the data at acid loadings less than 1.0 gm/100 gms carbon was excluded from the rate model computations. It also indicates that application of the model at low acid loadings would cause a significant underestimation of the sorption rate.

Fluid Bed SO_2 Sorption Experiments -

This section covers the pre-integral fluid bed sorption work that was done in the 6" and 18" diameter SO_2 sorbers. Objectives included demonstration of satisfactory mechanical operation and process performance, gathering of additional information on reaction rate and process characteristics, and completion of necessary developmental work in preparation for integral pilot plant operation.

6" Diameter Sorber -

Operation of a 6" diameter, eight stage fluid bed sorber provided the first test of the SO_2 sorption step under actual flue gas conditions of a slipstream from a 50 MW oil fired boiler. Successful demonstration of the 6" unit was an important achievement in development of the process. Operation of the 6" sorber provided valuable reaction rate data for comparison with the Westvaco rate model.

The 6" sorber runs offered the first opportunities to test the rate model in predicting the performance of an actual flue gas system. The data from six runs was processed to give average values of SO_2 concentration, acid loading and reaction rate on each stage of the reactor. These average values are given with the run conditions in Appendix A-5. The y_{SO_2} and X_V values were then used in the Westvaco rate equation to calculate predicted rates for comparison with the experimental rates. The results of the comparison are presented in Table 21. The predicted rates average about 14% below the experimental rates.

Figure 37. Differential SO2 sorption rate versus H2SO4 loading for an SO_2 concentration of 2500 ppm at 150, 200, and 300°F

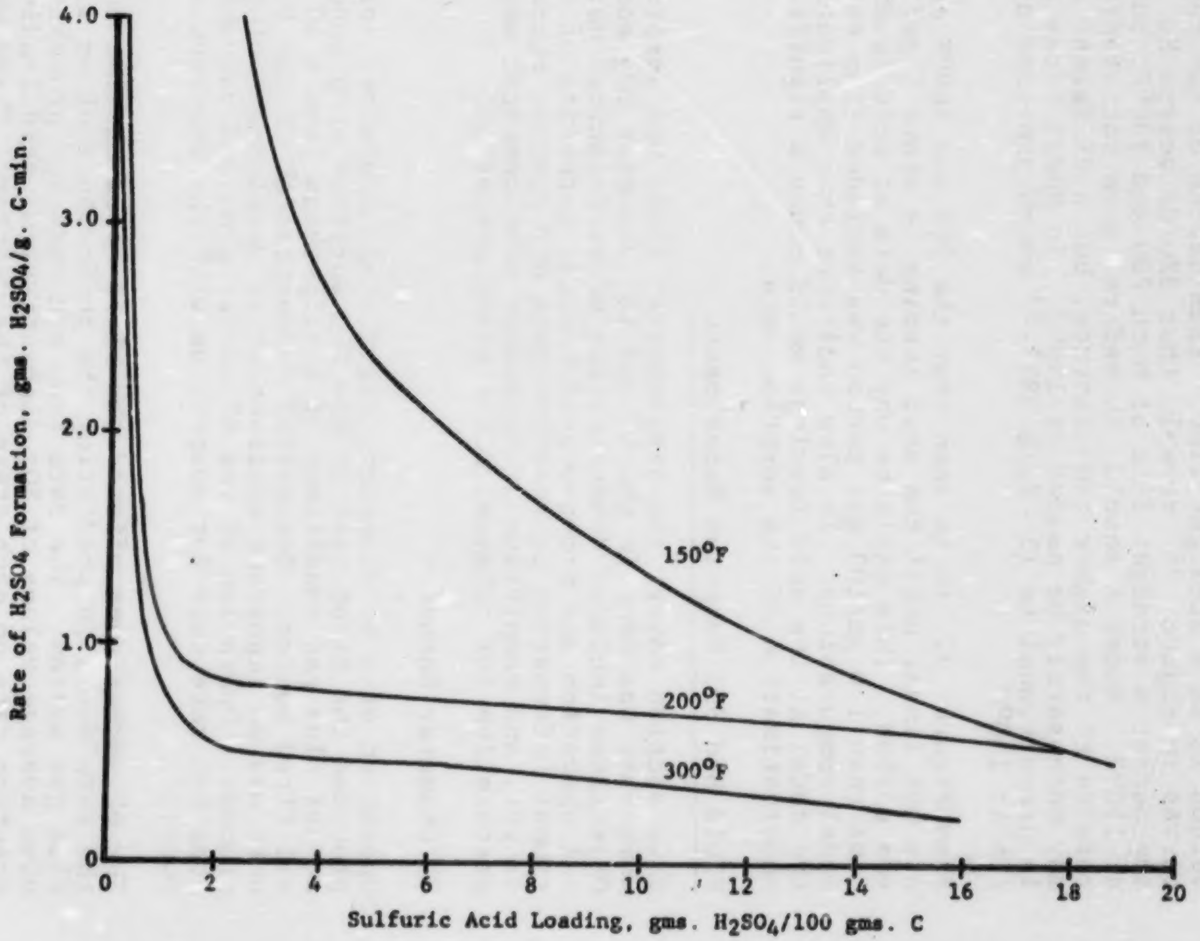


Table 21. COMPARISON OF RATES FROM 6" DIAMETER SORBER TO RATES CALCULATED FROM THE WESTVACO MODEL

Run*	Stage	Temperature, °F	gms Acid/gm Carbon	SO_2 Concentration, ppm	Sorption Rate x 10^3, #Acid/#Carbon-Min.	
					6 Inch**	Model***
SA-21	1	200	0.0213	251	0.76	0.72
	2		0.0426	425	0.76	0.84
	3		0.0662	607	0.84	0.90
	4		0.0920	808	0.92	0.93
	5		0.1178	1,018	0.92	0.93
	6		0.1480	1,247	1.08	0.89
	7		0.1817	1,507	1.20	0.82
SA-23	1	200	0.0087	46	0.35	0.38
	2		0.0260	183	0.71	0.63
	3		0.4777	388	0.89	0.80
	4		0.0703	621	0.92	0.90
	5		0.0954	872	1.03	0.95
	6		0.1241	1,155	1.17	0.95
	7		0.1562	1,475	1.31	0.92
SA-26	1	200	0.0170	132	0.72	0.58
	2		0.0377	324	0.88	0.78
	3		0.0583	534	0.88	0.89
	4		0.0817	758	0.99	0.95
	5		0.1068	1,005	1.07	0.98
	6		0.1346	1,274	1.18	0.96
	7		0.1660	1,576	1.33	0.91
SA-22	1	200	0.0308	1,306	1.24	1.36
	2		0.0607	1,612	1.21	1.36
	3		0.0888	1,904	1.13	1.32
	4		0.1214	2,210	1.32	1.25
	5		0.1531	2,535	1.28	1.16
	6		0.1875	2,868	1.39	1.03
	7		0.2274	3,242	1.61	0.86
SA-25	1	200	0.0140	484	0.56	0.52
	2		0.0307	644	0.67	0.56
	3		0.0464	813	0.63	0.59
	4		0.0657	996	0.77	0.60
	5		0.0832	1,187	0.70	0.61
	6		0.1043	1,388	0.84	0.60
	7		0.1279	1,621	0.95	0.59
SA-24	1	200	0.0241	1,219	0.96	0.79
	2		0.0482	1,502	0.96	0.80
	3		0.0738	1,795	1.02	0.80
	4		0.1002	2,101	1.05	0.78
	5		0.1282	2,420	1.11	0.74
	6		0.1530	2,731	0.99	0.70
	7		0.1981	3,142	1.79	0.59

*Inlet gas compositions for the runs are given in Appendix B.

**Rate data from 6" diameter sorber.

***Rate data calculated from Westvaco Model, Equation (27).

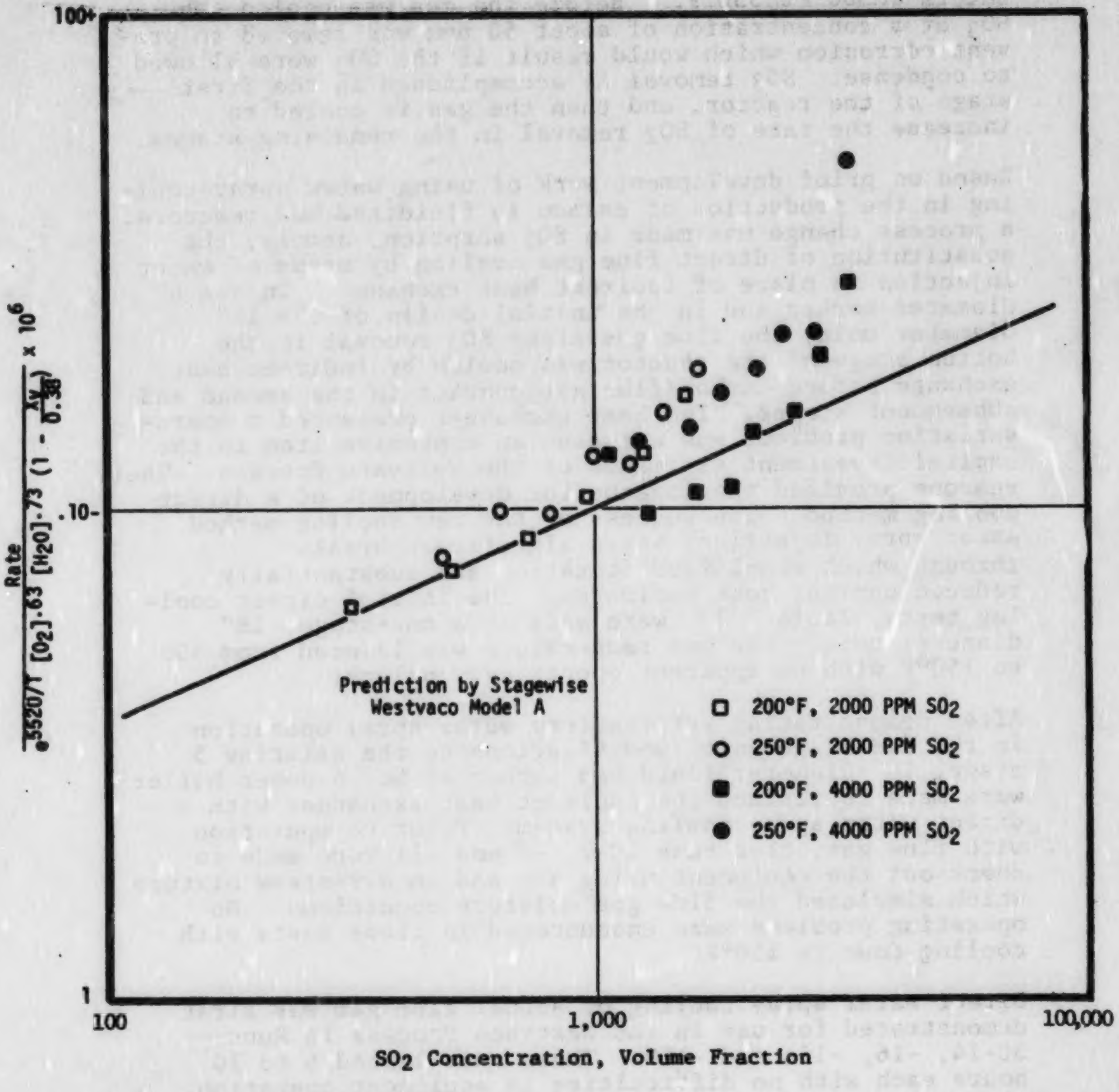
A graphical comparison of the rate model to the fluid bed rate data is given in Figure 38. Average experimental reaction rates are plotted versus SO_2 concentration, with the rate equation superimposed for comparison. The reaction rates in Figure 38 were obtained from the actual rates by dividing by all variable terms in the equation except y_{SO_2}. This mathematical comparison assumes that all differences then arise with the SO_2 concentration term in the model, which is not necessarily true but if large discrepancies had occurred, then additional analysis would have been required. The graph shows a reasonably good fit of the data by the model.

The rate model was also tested by using it in a design procedure to calculate the theoretical number of stages required for each run. The detailed derivation of the design procedure is given in Appendix C-1. The results of this comparison are shown in Table 22. The average predicted number of stages is 9.9 compared to the actual 8, which is an over-estimation of 25%. The rate model, therefore, can be expected to yield conservative estimates of reactor size.

Table 22. COMPARISON OF PREDICTED NUMBER OF STAGES TO ACTUAL NUMBER FOR 6" SORBER RUNS

Run	Temperature, °F	Inlet SO2 Conc., ppm	Actual No. of Stages	Predicted No. of Stages Model A
SA-21	200	2000	8	9.2
SA-23	200	2000	8	8.5
SA-26	200	2000	8	10.1
SA-22	200	4000	8	9.3
SA-24	250	2000	8	11.6
SA-25	250	4000	8	10.4
		AVERAGE:	8	9.9

Figure 38. 6" sorber data - plot of corrected sorber rate using stagewise Westvaco Model A vs. SO_2 concentration showing curve predicted from differential bed studies



18" Diameter Sorber -

Operation of an 18" diameter sorber was the next step in development and provided additional process information. In the operation of an SO_2 sorber, the flue gas typically enters at 300°F to 350°F. Before the gas was cooled, the SO_3 at a concentration of about 50 ppm was removed to prevent corrosion which would result if the SO_3 were allowed to condense. SO_3 removal is accomplished in the first stage of the reactor, and then the gas is cooled to increase the rate of SO_2 removal in the remaining stages.

Based on prior development work of using water spray cooling in the production of carbon in fluidized bed reactors, a process change was made in SO_2 sorption, namely, the substitution of direct flue gas cooling by means of water injection in place of indirect heat exchange. In the 6" diameter sorber and in the initial design of the 18" diameter unit, the flue gas after SO_3 removal in the bottom stage of the reactor was cooled by indirect heat exchange before carbon/flue gas contact in the second and subsequent stages. The heat exchanger presented tempera-variation problems and was also an expensive item in the capital investment estimates of the Westvaco Process. These reasons provided the impetus for development of a direct cooling method. The success of the new cooling method, water spray injection, was a significant breakthrough which simplified operation and substantially reduced capital cost estimates. The initial direct cooling tests, Table 23 were made in a one-stage, 18" diameter unit. The gas temperature was lowered from 300 to 150°F with no apparent operating problems.

After demonstrating satisfactory water spray operation in the one stage unit, modifications to the existing 5 stage, 18" diameter fluid bed sorber at No. 6 power boiler were made to replace the indirect heat exchanger with a direct water spray cooling system. Prior to operation with flue gas, test runs SC-7, -8 and -11 were made to check out the equipment using air and an air-steam mixture which simulated the flue gas moisture conditions. No operating problems were encountered in these tests with cooling down to 150°F.

Direct water spray cooling of actual flue gas was first demonstrated for use in the Westvaco Process in Runs SC-14, -16, -16A and -16B. These runs lasted 6 to 10 hours each with no difficulties in equipment operation. In an extended demonstration run, SA-32, mechanical problems were encountered that were unrelated to the water spray system, but despite the problems a total

Table 23. WATER SPRAY COOLING TESTS MADE IN PILOT FLUID BED REACTORS WITH SIMULATED AND ACTUAL FLUE GAS

RUN NUMBER	UNIT USED	NUMBER OF STAGES	TOTAL CARBON BED HEIGHT (SETTLED) INCHES	INLET GAS TEMP. °F	STAGE TEMPERATURE °F				LINEAR GAS VELOC. FT/SEC	H2O SPRAY RATE #/HR.	TOTAL GAS FLOW RATE, CFH @ 70°F	INLET O2 ANAL., VOL. %	INLET H2O ANAL., VOL. %	SULFUR DIOXIDE ANALYSIS, PPM					CARBON PRECURSOR SKID NO. AND CHAS. NO.	CARBON ACID LOADING LBS. SO2/ 100 LBS. C		CARBON RATE #C/HR.
					#1	#2	#3	#4						INLET	STAGE 1	STAGE 2	STAGE 3	OUTLET		INLET	OUTLET	
SC-1	18" Dia. Fluid Bed One-Stage Unit	1	6	300	200	---	---	---	2.9	23.4	14,070	10	10	---	---	---	---	---	WV-W	---	---	0
SC-2		1	6	"	178	---	---	---	3.1	31.2	14,900	"	"	---	---	---	---	---	"	---	---	0
SC-3		1	6	"	149	---	---	---	3.1	43.0	16,500	"	"	---	---	---	---	---	"	---	---	0
SC-4		1	7.5	"	152	---	---	---	3.1	33.2	16,500	"	"	---	---	---	---	---	"	---	---	0
SC-5		1	9	"	149	---	---	---	3.1	27.4	16,500	"	"	---	---	---	---	---	"	---	---	0
SC-7	18" Dia. Fluid Bed SO2 Sorber	4	15.5**	380	350	242	250	240	3.1	10	14,830	Air	~4	---	---	---	---	---	96257, C-71-98	0	0	23
SC-8		4	15.5**	330	317	140	150	150	2.6	37.2	14,430	"	~4	---	---	---	---	---	"	0	0	23
SC-11		4	15.5**	327	310	190	183	175	2.9	44.7	15,280	"	~12	---	---	---	---	---	"	0	0	23
SC-14		4	15.5**	310	295	175	180	175	3.0*	29.8	15,250	3.1	12.7	995	925	540	330	70	"	0	10.3	23.2
SC-15		4	15.5**	300	280	140	155	170	3.1*	45	16,230	3.1	12.7	880	---	---	---	170	"	4.1	13.7	19.2
SA-16A		4	15.5**	310	290	150	160	160	3.1*	40.2	16,200	3.1	12.7	1,125	1,070	560	460	160	"	8.7	20.9	20.2
SC-16B		4	15.5**	310	290	150	160	160	3.1*	40.2	16,200	3.1	12.7	1,100	---	---	---	55	96324, C-71-23	0	14.2	19.9
SA-32		4	15.5**	315	295	175	180	180	3.1*	34	16,767	3.1	12.9	2,200	2,088	1,511	1,008	522	96283, C-71-100	0	11.9	32.9

*Based on average temperature of Stages 2, 3 and 4.
**Excluding carbon on bottom stage at about 300°F (about 3 inches carbon).

operating time of 29 hours was achieved, and the water spray cooling system subsequently was declared a success.

The advantages of using water spray cooling instead of indirect heat exchange are summarized as follows:

1) A savings on the order of 25% in the capital investment estimated for the Westvaco Process

2) Temperatures as low as 150°F can be achieved which would be difficult using a heat exchanger because of moisture condensation at cooling surfaces or very large surface areas for heat transfer.

3) The small amount of moisture from the water spray increases the rate of SO_2 removal.

4) Better control of the column temperature has been realized with water spray cooling.

Additional runs were made in the 18" diameter sorber in order to produce acid loaded carbon needed for the sulfur generation and sulfur stripping experiments. These runs contributed valuable information about the unit's operating characteristics and they also led to early recognition of problem areas, thereby providing a basis for necessary corrective measures and improvements to increase operational reliability.

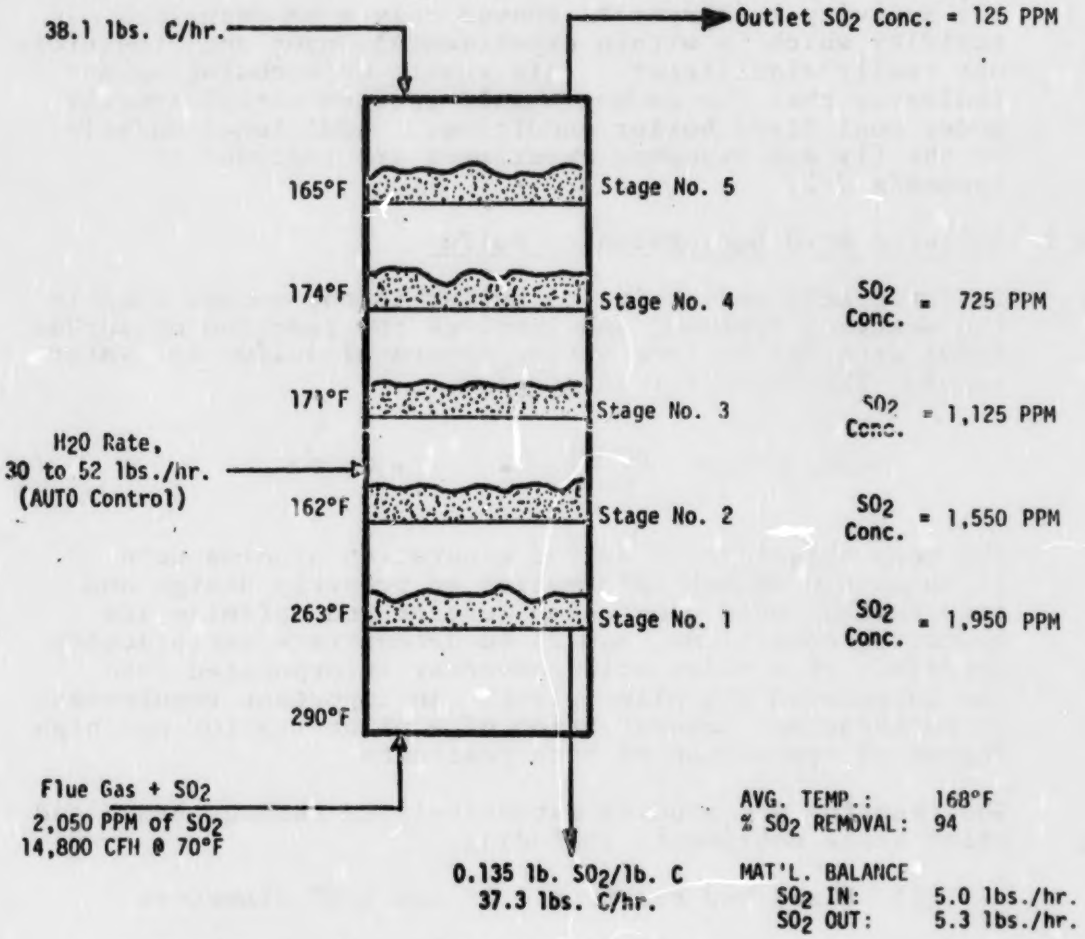
The summary for a typical sorption run, SA-32, is given in Figure 39. Temperature and SO_2 concentration profiles through the column are shown. Average column temperature for Stages 2 to 5 was 168°F. The SO_2 removal was 94%, and the material balance agreed within 6%.

Effect of Fly Ash on Carbon SO_2 Activity -

Application of the Westvaco SO_2 Process in the flue gas desulfurization area would involve both coal and oil fired boilers. One difference between the two is the significantly higher fly ash concentration in the flue gas from coal fired boilers. Pilot plant SO_2 sorption work has been conducted using flue gas from an oil fired boiler only, so that the results are not necessarily applicable under coal fired boiler conditions.

Of greatest concern is the possibility that prolonged exposure of activated carbon to high fly ash concentrations may reduce the carbon's SO_2 activity. This was

Figure 39. Summary for flue gas run (run SA-34); 18" diameter SO_2 sorber; water sprays to control temperature



38.1 lbs. C/hr.
Outlet SO2 Conc. = 125 PPM
165°F
Stage No. 5
174°F
Stage No. 4
SO2 Conc. = 725 PPM
171°F
Stage No. 3
SO2 Conc. = 1,125 PPM
H2O Rate, 30 to 52 lbs./hr. (AUTO Control)
162°F
Stage No. 2
SO2 Conc. = 1,550 PPM
263°F
Stage No. 1
SO2 Conc. = 1,950 PPM
290°F
Flue Gas + SO2
2,050 PPM of SO2
14,800 CFH @ 70°F
0.135 lb. SO2/lb. C
37.3 lbs. C/hr.
AVG. TEMP.: 168°F
% SO2 REMOVAL: 94
MAT'L. BALANCE
SO2 IN: 5.0 lbs./hr.
SO2 OUT: 5.3 lbs./hr.

investigated in a bench scale experiment in which recycled carbon was exposed to fly ash laden air for a period of 5 days. The ash content of the carbon was measured each day and the SO_2 activity was measured before and after. The ash content did not increase above the initial level corresponding to the inherent ash content of the carbon, which is typically in the range of 4-1/2 to 5% by weight. SO_2 activity measurements showed only a 6% drop in activity which is within experimental error and, therefore, not really significant. This result is encouraging and indicates that the carbon should perform satisfactorily under coal fired boiler conditions. Additional details of the fly ash exposure experiment are included in Appendix J-2.

5.2.2 Sulfuric Acid Conversion to Sulfur

Sulfuric acid conversion to sulfur is the second step in the Westvaco Process, and involves the reaction of sorbed H_2SO_4 with H_2S to form sorbed elemental sulfur and water vapor. The overall reaction is:

$$H_2SO_4 + 3\ H_2S \xrightarrow[\text{Carbon}]{\text{Activated}} 4\ S + 4\ H_2O\uparrow \qquad (6)$$

The main objective of sulfur generation studies were: 1) to obtain enough information to properly design and construct an acid conversion reactor and optimize its operating conditions, and 2) to demonstrate satisfactory operation of a pilot acid converter incorporated into the integrated SO_2 pilot plant. An important requirement in satisfactory demonstration of a pilot reactor was high degree of conversion of both reactants.

The reaction was studied extensively in various bench and pilot scale equipment, including:

1) Fixed bed reactors - 1" and 1.6" diameters

2) One stage, 4" diameter fluid bed batch reactor

3) 8 stage, 4" diameter fluid bed glass column counter current reactor

4) 8 stage, 4" diameter fluid bed reactor (eventually used as sulfur stripper/H_2S generator in integral pilot plant)

5) Moving bed reactors - 1.5" and 8" diameters (8"0 eventually used as sulfur generator in integral pilot plant).

A rate expression was found to represent kinetic data measured in a one stage fluid bed reactor. The kinetic data was incorporated into a reactor design procedure. The important variables in the reaction rate are temperature, acid concentration on carbon, and the gas concentrations of H_2S and H_2O.

Experimental studies indicated that the required high conversions of both H_2S and H_2SO_4 were not possible at the space velocities obtainable in a 6"Ø fluid bed reactor that initially was considered for use in the integrated pilot plant. Subsequent tests in a 1.5" diameter bench scale moving bed reactor indicated that a moving bed was better suited for integral operation of the pilot plant. A pilot scale 8" diameter moving bed unit was then designed and tested; and satisfactory performance was demonstrated.

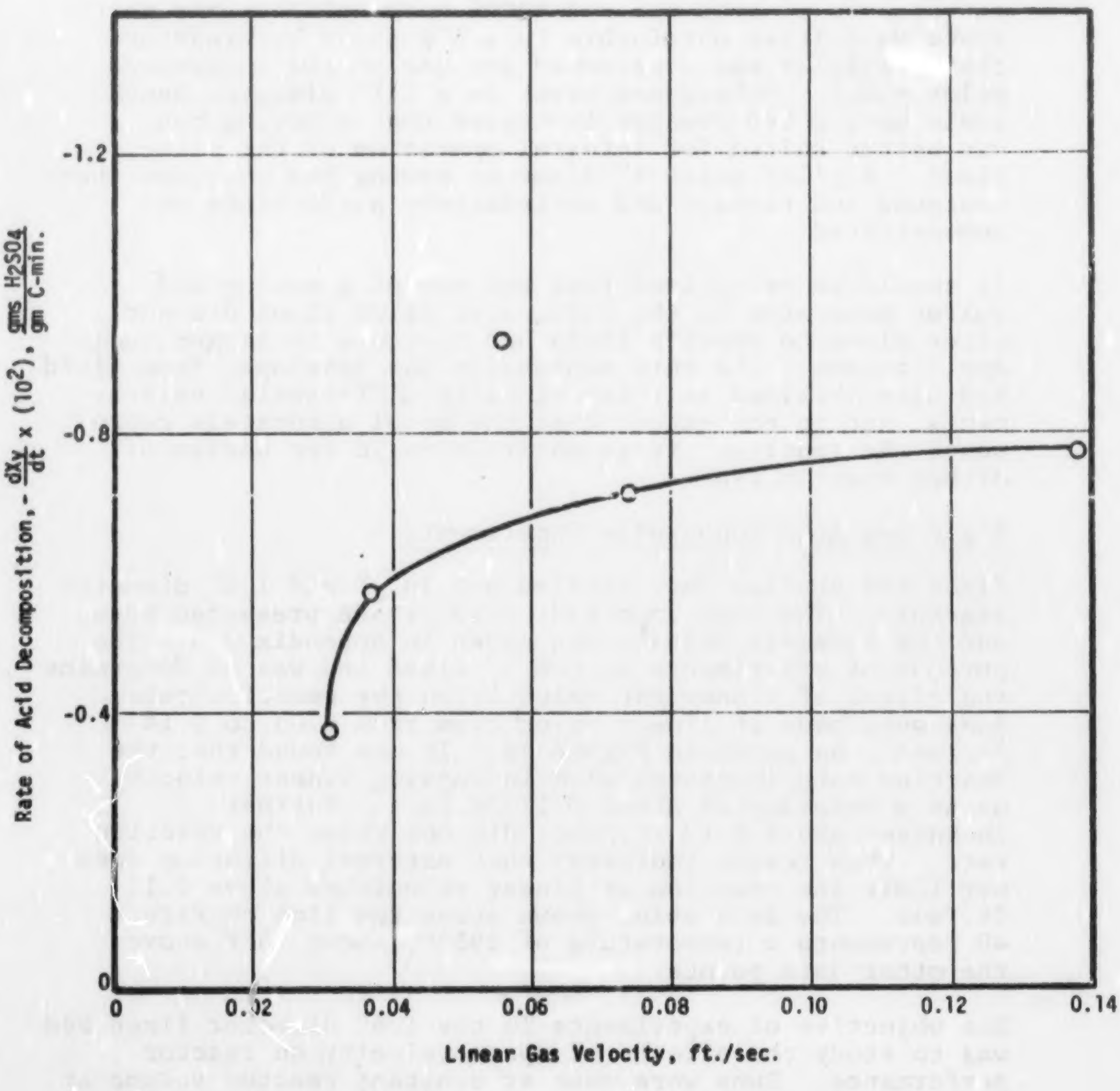
It should be recognized that the use of a moving bed sulfur generator in the integrated pilot plant did not alter plans to specify fluid bed reactors in larger scale applications. The rate expression was developed from fluid bed data obtained in a set of batch differential experiments, and to the extent that the model accurately represents the reaction, it is entirely valid for design of either reactor type.

Fixed Bed Acid Conversion Experiments -

Fixed bed studies were carried out in 1" and 1.6" diameter reactors. The more important results are presented here, and the complete results are given in Appendix J-3. The purpose of experiments in the 1" fixed bed was to determine the effect of linear gas velocity on the reaction rate. Runs were made at linear velocities from 0.03 to 0.14 ft./sec., as shown in Figure 40. It was found that the reaction rate increased with increasing linear velocity up to a velocity of about 0.12 ft./sec. Further increases above 0.12 ft./sec. did not raise the reaction rate. This result indicates that external diffusion does not limit the reaction at linear velocities above 0.12 ft./sec. The data point shown above the line on Figure 40 represents a temperature of 395°F, about 75°F above the other data points.

The objective of experiments in the 1.6" diameter fixed bed was to study the effects of space velocity on reactor performance. Runs were made at constant reactor volume at space velocities from 100 to 1,000 $hr.^{-1}$. The inlet gas composition was held constant throughout each run, and the outlet H_2S concentration was monitored continuously to determine the time at which H_2S breakthrough occurred. The results showed almost immediate H_2S breakthrough at

Figure 40. Effect of linear gas velocity on rate of sulfuric acid decomposition



space velocities above 300 hr.$^{-1}$, but at 100 hr.$^{-1}$ breakthrough did not occur until 130 minutes. Overshadowing these results, however, were the implications of the temperature rise that occurred in the bed due to the exothermic (-65 kcal/mole acid) heat of reaction. The same problem occurred to a lesser degree in the 1" fixed bed runs. A temperature rise of 135°F was recorded in 3 out of 8 runs in the 1.6" diameter bed. The most important result of these experiments, therefore, was to clearly demonstrate the unsuitability of a fixed bed reactor in kinetic studies of the sulfur generation reaction. The temperature control which is necessary to obtain useful data could not be achieved in a fixed bed unit.

Fluid Bed Rate Studies -

The effects of temperature and H_2S concentration on the rate of reaction were studied in an 8 stage, 4" diameter fluidized bed reactor constructed from flanged sections of glass pipe. Each stage had 4 inch overflow weirs for a typical carbon bed depth of 2.5 inches/stage, so that the total settled bed depth was typically 20 inches of carbon. Experiments were run at temperatures of 250, 275, 300, 325 and 350°F, and at inlet H_2S concentrations from 12% to 42%. Average steady state conditions for each run are shown in Table 24.

The overall rate of sulfuric acid decomposition was calculated for each run based on both gas and carbon analyses for sulfur compounds. A comparison of the results given in Table 25 shows that reaction rates calculated from carbon analyses are about 20% lower than those determined from gas analyses. In the following discussion of results, the rates based on carbon analyses are used because they are considered more reliable and are more conservative.

The rate of acid decomposition increases steadily with increasing temperature, rising from 0.007 lb. acid/lb. C-min. at 250°F to 0.20 at 325°F. The rate levels out around 325°F and is about the same at 350°F as at 325°F. Figure 41 shows a plot of rate versus temperature.

An important temperature dependent effect begins to appear at 300°F which effectively places an upper limit of 325 to 350°F on the practical operating temperature range. This refers to the evolution of reactant acid in the form of SO_2 in the outlet gas. Although the exact mechanism is uncertain, the net result is that acid converts to SO_2 at the expense of complete acid reduction to elemental sulfur.

Table 24. EXPERIMENTAL CONDITIONS AND RESULTS FOR SULFUR GENERATION EXPERIMENTS IN AN EIGHT STAGE, 4" DIAMETER FLUIDIZED BED REGENERATOR

Run Number and Purpose		Temperature °F	Inlet Gas Flow Rate,		Gas Composition*, Volume %			Total Solid Flow** Rate, R_{Ti} lbs./hr.	Sulfur Analysis on Inlet Solid, Wt. %	
					Inlet	Outlet			Inlet***	Outlet
			N_2	H_2S	H_2S	H_2S	SO_2		P_{si}	P_{so}
Estimation of Requirements for Total Acid Conversion	SG-27	300	285	96	24	10	0	53	5.6	13.0
	SG-28	300	302	108	27	17.8	0	61	5.6	11.5
	SG-29	300	302	108	27.2	11.2	0.12	58	5.0	12.7
	SG-30	300	334	72	17.0	7.6	0.25	56	5.1	11.0
	SG-31****	300	320	108	25.6	13.5	0.12	61	14.5	22.4
Effect of Temperature	SG-33	300	283	130	27.7	15.7	0	61	6.1	14.2
	SG-34	250	304	131	30.4	24.4	0	64	6.0	9.4
	SG-35	275	294	126	31.5	20	0	64	6.1	11.3
	SG-36	325	276	118	30.8	6.0	0.35	56	6.1	18.7
	SG-37	350	267	114	30		2.6	54	6.2	18.0
Effect of H_2S Conc.	SG-38	350	267	114	32.0	8.8	1.3	53	6.4	18.3
	SG-39	325	276	119	31.8	6.0	2.0	55	6.0	18.0
	SG-40	325	236	158	42.0	12.0	1.6	76	5.5	17.0
	SG-41	325	362	37	12.0	3.1	1.6	18	5.7	14.4

*As determined by gas chromatograph.

**Total solid flow rate of the carbon plus its sorbed sulfur compounds.

***Except for SG-31 the per cent sulfur is present only as sorbed acid.

****Inlet material for this run was a blend of the partially converted loaded carbon from Runs SG-28 and -29 which originally had an average acid loading of approximately .19 # H_2SO_4/# C.

Table 25. OVERALL RATES OF ACID DECOMPOSITION AND CONVERSION TO SULFUR FOR THE REACTION $3\ H_2S + H_2SO_4 \longrightarrow 4\ S + 4\ H_2O$ IN AN EIGHT STAGE, 4" DIAMETER REGENERATOR

Run No.	Temp. °F	Inlet Acid Loading $\#H_2SO_4/\#C$	Inlet H_2S %	Outlet SO_2 %	Conv. to S***, %	Overall Rate of Reac., $\#\ H_2SO_4/\#C$-min.	
						Gas Analysis*	Carbon Analysis**
SG-27	300	0.21	24	0	43	$1.52(10^{-2})$	$1.2(10^{-2})$
SG-28	300	0.21	27	0	34	$1.05(10^{-2})$	$1.1(10^{-2})$
SG-29	300	0.18	27.2	0.12	51	$1.87(10^{-2})$	$1.34(10^{-2})$
SG-30	300	0.19	17	0.25	39	$1.08(10^{-2})$	$1.06(10^{-2})$
SG-31	300	****	25.6	0.12	115	$1.40(10^{-2})$	----
SG-33	300	0.24	27.7	0	46	$1.39(10^{-2})$	$1.62(10^{-2})$
SG-34	250	0.23	30.4	0	18	$0.71(10^{-2})$	$0.66(10^{-2})$
SG-35	275	0.24	31.5	0	24	$1.33(10^{-2})$	$0.88(10^{-2})$
SG-36	325	0.24	30.8	0.35	62	$2.83(10^{-2})$	$2.0(10^{-2})$
SG-37	350	0.24	30	2.6	66	----	$2.08(10^{-2})$
SG-38	350	0.25	32	1.3	61	$2.54(10^{-2})$	$1.96(10^{-2})$
SG-39	325	0.23	31.8	2.0	66	$2.95(10^{-2})$	$2.04(10^{-2})$
SG-40	325	0.21	42	1.6	65	3.24(10)	$2.56(10^{-2})$
SG-41	325	0.22	12	1.6	50	1.04(10)	$0.48(10^{-2})$

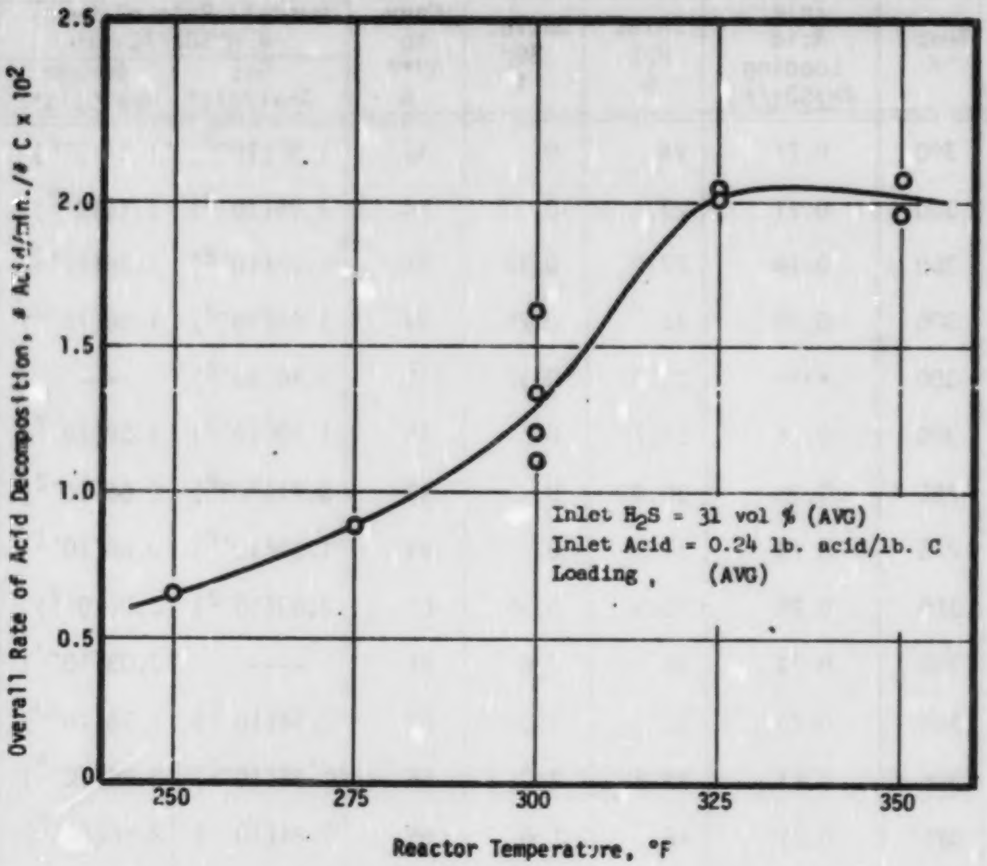
*Based on gas analysis using a chromatograph.

**Based on carbon analysis using a combustion analysis technique.

***Calculated from experimental data.

****Inlet material for this run was a blend of partially converted loaded carbon from Runs SG-28 and -29 which originally had an average acid loading of approximately .19 lb. acid/lb. C.

Figure 41. Effect of temperature on the rate of conversion of sorbed sulfuric acid to elemental sulfur



The following two-step reaction sequence is believed to be the most probable mechanism for conversion of acid to elemental sulfur:

$$H_2SO_4 + H_2S \longrightarrow SO_2 + S + 2\ H_2O \qquad (35)$$

$$SO_2 + 2\ H_2S \longrightarrow 3\ S + 2\ H_2O \qquad (36)$$

$$H_2SO_4 + 3\ H_2S \longrightarrow 4\ S + 2\ H_2O \qquad (37)$$

Because SO_2 is an intermediate in these reactions, its presence in the outlet gas could be expected under at least some reaction conditions.

The results in Table 25 show that the outlet gas SO_2 concentration increases above 300°F, rising from about 0.15% at 300°F to 2% at 350°F. The 2% figure represents about a 20% conversion of acid to SO_2. The results indicate that operating temperature above 325°F should be avoided in order to minimize SO_2 formation.

The reaction rate also increases with increasing H_2S concentration, as seen most clearly by inspecting the results of SG-39, -40 and -41. Further discussion of the H_2S concentration effect is postponed to the next section on rate model development.

These experiments also provided an average reaction rate for anticipated process conditions to be used in preliminary design work. To obtain the average rate over a wide set of operating conditions it was necessary to obtain complete acid conversion, and this was accomplished by passing the carbon through the reactor twice. The partially reacted carbon product from Runs SG-28 and -29 was combined and fed to the reactor again in SG-31. The results of these experiments indicate an overall average reaction rate to complete conversion under anticipated conditions of about 0.01 lb. acid/lb. C-min.

Rate Model Development -

A series of differential batch experiments was carried out in a 4" diameter fluidized bed reactor in order to obtain data to develop a rate expression. In each run a small batch of acid loaded carbon was fluidized with reactant gas at constant conditions of temperature and gas concentration. Samples of carbon were removed at intervals for analysis, thereby providing reaction data as a function of time for total sulfur content and acid loading. Space velocity was sufficient that the inlet and outlet reactant gas concentrations were essentially identical. This justified the differential reactor assumption.

The variables studied were temperature, acid loading, sulfur loading, and the gas concentrations of H_2S and H_2O. The conditions for each run are presented in Table 26. Temperatures of 250, 300 and 325°F were tested, and H_2S

Table 26. EXPERIMENTAL CONDITIONS FOR DIFFERENTIAL SULFUR GENERATION RUNS

Carbon Used:	SA-27-A (335-365 min.)
Virgin Procursor:	Skid 96298
Residual S on Virgin Carbon:	0.6 wt. %
Carbon Density:	49.7 lbs./ft.^{3}
Linear Gas Velocity:	2 ft./sec.
Diluent Gas:	Nitrogen

Run Number	Gas Concentrations, Volume %		Nominal Bed Temperature, °F
	H_2S	H_2O	
DSG-24	4.4	0	250
DSG-25	14.1	0	250
DSG-26	25.4	0	250
DSG-41	4.4	10	250
DSG-27	5.3	0	300
DSG-28	10.0	0	300
DSG-29	15.0	0	300
DSG-30	20.8	0	300
DSG-31	31.6	0	300
DSG-32	5.3	30	300
DSG-33	5.3	20	300
DSG-34	5.3	10	300
DSG-35	5.0	0	325
DSG-36	9.1	0	325
DSG-37	18.2	0	325
DSG-38	26.4	0	325
DSG-39	37.6	0	325

concentration was varied over a range of 4 to 37%. The H_2O concentration was varied from 0 to 30%. The data from each run is given in Appendix A-11.

To evaluate the data the rate expression was assumed to be of the form:

$$\frac{dX_S}{dt} = k\, g_1(T)\, g_2(X_V)\, g_2(X_S)\, g_3(y_{H_2S})\, g_5(y_{H_2O}) \qquad (38)$$

The data was analyzed by stepwise and multiple regression methods and the following expression was obtained for experiments of an inlet water concentration of zero.

$$\frac{dX_S}{dt} = 23.6\, e^{-2644/T}\, y_{H_2S}^{0.58}\, X_V^{0.67} \quad \text{lbs. S/lb. C-min.} \qquad (39)$$

The sulfur loading (X_S) was found to have no observable effect on the rate, or at least the effect could not be isolated from the effect of the acid loading (X_V), so that $g(X_S) = 1$. The function of water, $g(y_{H_2O})$, was not determined explicitly due to the nature of this variable's effect on the reaction, and consequently Equation (39) applies only for $y_{H_2O} = 0$. Equation (39) fits the differential data reasonably well as shown in Figure 42. A statistical analysis showed the average difference between the model and the differential data to be 17% with a maximum difference of 50%.

Extension of the rate model to situations where water vapor is present required some provision for the effect of this variable. Figure 43 shows the effect that water vapor has on the reaction rate. The data indicate that the rate decreases sharply as y_{H_2O} increases from 0 to 20%, but that there is no further decrease above 20%. There is a factor of about 6 between the rates at 0 and 20% water vapor.

The rate model was tested against the results of sulfur generation runs in the 4" diameter fluid bed pilot regenerator (subsequently described in this section) by using it in a design equation to calculate predicted reactor volumes. In conducting the evaluation, various representations of

Figure 42. Comparison of the sulfur generation rate model to the experimental data for 250 to 325°F

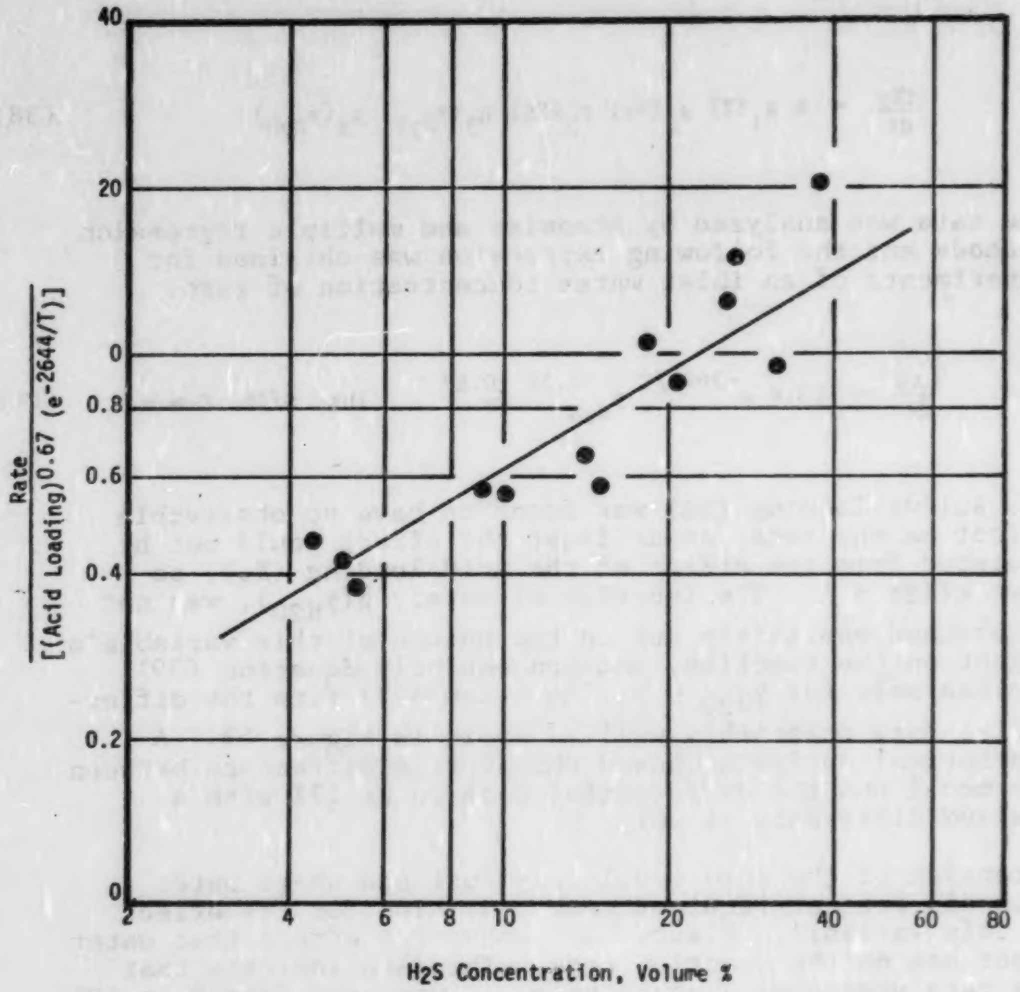
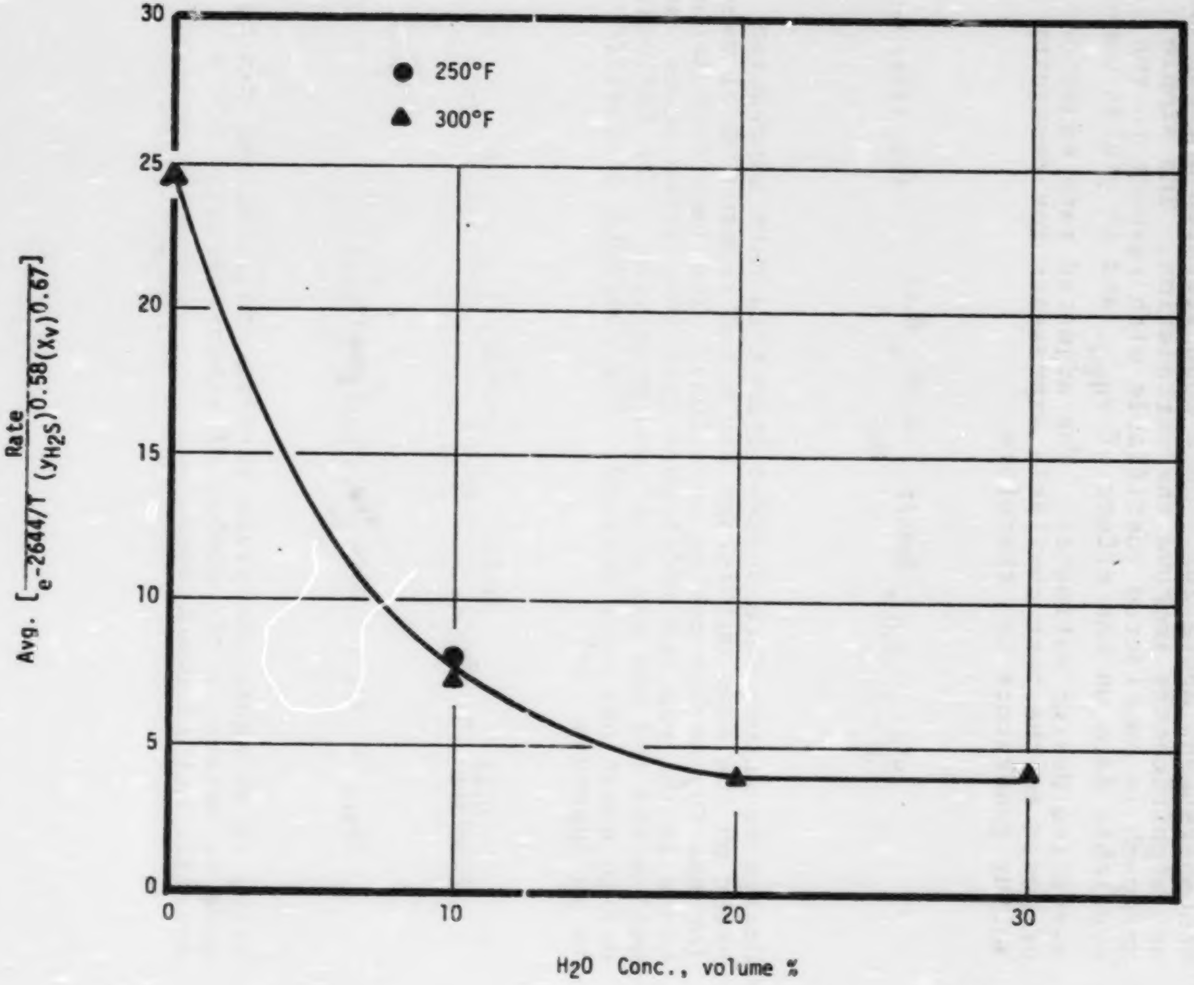


Figure 43. Effect of H2O concentration on rate of sulfur generation



$g(y_{H2O})$ were tried in an attempt to obtain the best correlation between actual and predicted reactor volumes. The approach which proved most successful was to take a conservative rate constant adjusted by a factor of 6 for H_2O concentrations above 20%. More sophisticated methods did not significantly improve the correlation. The simple approach is considered justifiable with respect to the available data on the effect of y_{H2O}, and it yields conservative design estimates. The adjusted rate equation proposed as the best available expression for designing sulfur generators is, therefore,

$$\frac{dX_S}{dt} = 3.8\, e^{-2644/T}\, y_{H_2S}^{\,0.58}\, X_v^{\,0.67} \qquad \text{lbs. S/lb. C-min.} \tag{40}$$

Design equations were derived from this rate expression based on the same multistage fluid bed reactor model used for the SO_2 sorber design equations. The important assumptions in the reactor model were that the carbon phase was well-mixed and the gas phase was plug flow. The following design equations were derived. The complete derivation is in Appendix A-9.

$$(Y_{H_2S})_{j+1}^{0.42} = (Y_{H_2S})_j^{\,0.42} - 15.8\, e^{-2644/T}\, hD^2 (XV_j)^{0.67}/q_T \tag{41}$$

$$XV_{j+1} = XV_j + 0.0846\, \frac{q_T}{R_c} \left[(Y_{H_2S})_j - (Y_{H_2S})_{j+1} \right] \tag{42}$$

Using these equations, plate-to-plate calculations can be made to determine the number of stages required for a specific set of conditions.

Fluid Bed Studies in 4" Diameter Pilot Regenerator To Determine Adequacy of Existing 6" Diameter Reactor as Pilot Sulfur Generator -

Experiments were carried out in the 8 stage, 4" diameter fluid bed pilot regenerator to determine whether the existing 6" diameter SO_2 sorber would make a satisfactory sulfur generator for the integrated pilot plant. The primary question was whether high conversion of both reactants could be obtained in the 6" diameter reactor. The goal was set at 99% acid conversion to sulfur at the maximum H_2S utilization at the space velocities possible in the existing 6" diameter reactor. The goal of 99% conversion of acid to sulfur was considered necessary during this period in development in order to avoid disruptions caused by unreacted acid entering the next step of regeneration. Later results from integrated operation showed that unreacted acid could be tolerated, but this was not known at the time decisions were made concerning adequacy of the 6" unit as a sulfur generator.

Achievement of 99% conversion of acid to sulfur was expected to be a difficult goal because the inlet H_2S concentration would have to be kept fairly low due to fluidization requirements in the 6" diameter unit and in order to obtain acceptable H_2S utilization. In fact, the stoichiometric H_2S concentration required for complete acid conversion at 100% H_2S utilization was only about 6% for the 6" diameter unit. This concentration was based on the anticipated sulfuric acid feed rate for integral operation, which determined the stoichiometric H_2S feed requirement, and on the volumetric gas flow rate necessary for proper fluidization in the 6" reactor, which determined the degree of dilution.

The experiments in the 4" diameter unit were designed to simulate the anticipated conditions in the 6" unit as closely as possible, but the conditions could not be simulated with complete accuracy due to a difference in total carbon bed depth between the two reactors. The 6" unit's planned bed depth was greater by a factor of 1.7 to 2.3 depending on the length of the overflow weirs, so that simulation of carbon residence time in the 4" unit required a reduction in the carbon feed rate per unit area to attempt to compensate for lower bed depth. As a consequence of the reduced carbon feed rate per unit area, the stoichiometric H_2S concentration was lower for the simulation runs. The lower bed depth in the 4" unit also caused a higher space velocity, since linear gas velocity was held constant. These two inaccuracies in simulation--higher space velocity and lower stoichiometric H_2S concentration--had a negative effect on conversion of reactants. Therefore, the results of the simulation experiments were conservative with respect to the likely performance of the 6" unit.

The conditions and results of the experiments are presented in Table 27. The runs were made at carbon feed rates of 9.8 and 6.3 lbs./hr. to provide carbon residence times of 32 and 50 minutes, respectively. Inlet acid loading was about 0.21 lb. acid/lb. C. Average column temperature was about 290°F in most experiments. Lower temperatures, about 260°F, were tried in a few runs. Linear gas velocity was 2.0 ft./sec. The inlet H_2S concentration ranged from 3.6% to 29.8% and the H_2S feed rate ranged from 1 to 5 times the stoichiometric requirement for complete acid conversion. Space velocity was 2800 to 3000 $hr.^{-1}$.

The main conclusion of the experiments was that the goal of 99% acid conversion to sulfur with high utilization of H_2S was not attainable under the 6" diameter unit conditions. The highest H_2S utilization, 72%, was achieved in Run SG-55 at a H_2S feed rate of 1.05 times the stoichiometric requirement, with an acid conversion to sulfur of 63%. At higher H_2S feed rates the H_2S utilization was lower, falling to about 50% at a ratio of 1.6, 40% at 2.2, and 30% at 4 with acid conversions to sulfur of 73, 85, and 90%, respectively.

In discussing the conversion of H_2SO_4, it is important to note that in addition to forming the desired elemental sulfur product, a fraction of the acid can react to form SO_2 that is evolved in the outlet gas of the acid conver converter. This reaction was observed in the experiments. The results show that the percent acid conversion was about the same for all runs, falling between 92% and 97%. The conversion to sulfur, however, ranged from 61 to 90%; and the amount of acid converted to SO_2 varied from 0 to 43%. Inlet H_2S concentration appeared to be the main determinant of the product distribution between sulfur and SO_2. As H_2S concentration was increased, conversion to sulfur also increased, and evolution of SO_2 decreased. The effects of inlet H_2S concentration on acid conversion to sulfur and SO_2 evolution are shown in Figures 44 and 45, respectively.

In order to obtain 90% acid conversion to sulfur, an inlet H_2S concentration of 20 to 30% was required, which represented a H_2S excess of 3 to 5 times the stoichiometric requirement and yielded a H_2S utilization below 30%. Experiments in which higher H_2S utilization was sought

Table 27. SUMMARY OF SULFUR GENERATION RESULTS

RUN NO.	COLUMN TEMP., °F		CARBON INLET STREAM			GAS INLET STREAM			CARBON OUTLET STREAM				GAS OUTLET STREAM						S BALANCE, LBS.		ACID DECOMP %	CONV TO S %	ACID DECOMP. RATE, #ACID/#C-MIN.	SPACE VELOC. HR.$^{-1}$
						GAS* FLOW CFH @ 70°F	H_2S CONC.		ACID LOAD., #ACID/#C	S LOAD., #S/#C		WT. FINES #C/HR	COMPOSITION**, VOLUME %				SO_2 EVOL. % IN ACID	H_2S UTIL. % OF INLET						
	AVG	RANGE	C RATE, #C/HR	RES. TIME MIN.	ACID LOAD., #ACID/#C		VOL. %	TIMES STOICH		THEO.	ACT.		H_2S	SO_2	H_2O	N_2			IN	OUT				
SG-55	294	275-312	9.8	32	0.215	438	6.1	1.05	0.015	0.282	0.178	---	1.8	0.79	7.0	90.6	43.0	72	2.96	2.87	98.0	63	4.27(10^{-3})	2,850
SG-57	295	276-315	"	"	"	439	9.6	1.66	0.012	"	0.206	---	4.4	0.49	7.3	87.7	27.5	52	4.28	4.12	94.4	73	4.94(10^{-3})	2,860
SG-64	286	270-303	"	"	"	439	9.6	1.66	0.011	"	0.222	---	4.5	0.44	8.6	86.5	23.9	52	4.25	4.26	95.0	79	5.33(10^{-3})	2,860
SG-56	294	276-324	"	"	"	436	13.6	2.36	0.011	"	0.217	0.007	8.0	0.36	7.9	83.7	19.1	40	5.	5.45	95.0	77	5.21(10^{-3})	2,840
SG-62	291	271-316	"	"	"	435	12.8	2.22	0.011	"	0.239	---	7.3	0.30	8.9	83.5	16.4	41	5.37	5.22	95.0	85	5.74(10^{-3})	2,530
SG-65	253	242-270	"	"	"	435	13.4	2.32	0.017	"	0.236	---	8.0	0.16	6.6	85.2	8.7	39	5.62	5.49	92.0	84	5.66(10^{-3})	2,830
SG-58	296	270-313	6.3	50	"	438	3.6	0.92	0.013	"	0.171	0.006	1.5	0.50	6.2	91.8	43.9	57	1.78	2.00	93.0	62	2.64(10^{-3})	2,830
SG-59	290	270-311	"	"	"	438	6.3	1.62	0.012	"	0.197	---	2.6	0.35	7.8	89.2	30.0	56	2.79	2.50	95.0	70	3.04(10^{-3})	2,850
SG-60	280	250-303	"	"	"	437	10.4	2.67	0.013	"	0.230	---	5.0	0.17	10.0	84.8	14.6	49	4.25	3.60	94.0	82	3.55(10^{-3})	2,840
SG-61	284	263-297	"	"	"	435	13.1	3.45	0.012	"	0.240	---	8.0	0	8.0	84.0	0	37	5.20	4.63	94.0	85	3.70(10^{-3})	2,830
SG-66	280	236-297	9.8	32	0.200	464	10.7	2.15	0.009	0.261	0.207	---	4.8	0.46	6.4	88.3	30.9	54	4.83	4.34	95.5	79	4.97(10^{-3})	3,020
SG-67	269	237-303	"	"	0.209	443	21.7	3.74	0.005	0.272	0.240	---	15.2	0.09	8.0	76.7	5.2	30	8.90	8.4	97.6	88	5.76(10^{-3})	2,880
SG-68	290	242-320	"	"	0.208	435	29.8	5.13	0.008	0.271	0.245	---	22.0	0	7.6	70.4	0	26	11.5	10.5	96.3	90	5.88(10^{-3})	2,830
SG-69	260	228-273	"	"	0.207	456	22.6	4.29	0.010	0.269	0.239	---	15.3	0.07	8.6	76.0	4.2	29	9.26	6.61	95.0	89	5.73(10^{-3})	2,970
SG-70	262	225-281	"	"	0.211	461	8.4	1.58	0.014	0.275	0.205	---	3.8	0.17	5.5	90.5	9.6	55	8.94	3.36	93.2	75	4.92(10^{-3})	3,000

*Linear gas velocity is 1.9 - 2 ft./sec. at average column temperature.

**CO_2 and CO not detected in outlet gas.

Figure 44. Effect of inlet H_2S concentration on the per cent conversion to sulfur in simulation experiments using a 6" diameter fluid bed unit for integrated operation with an 18" diameter SO_2 sorber

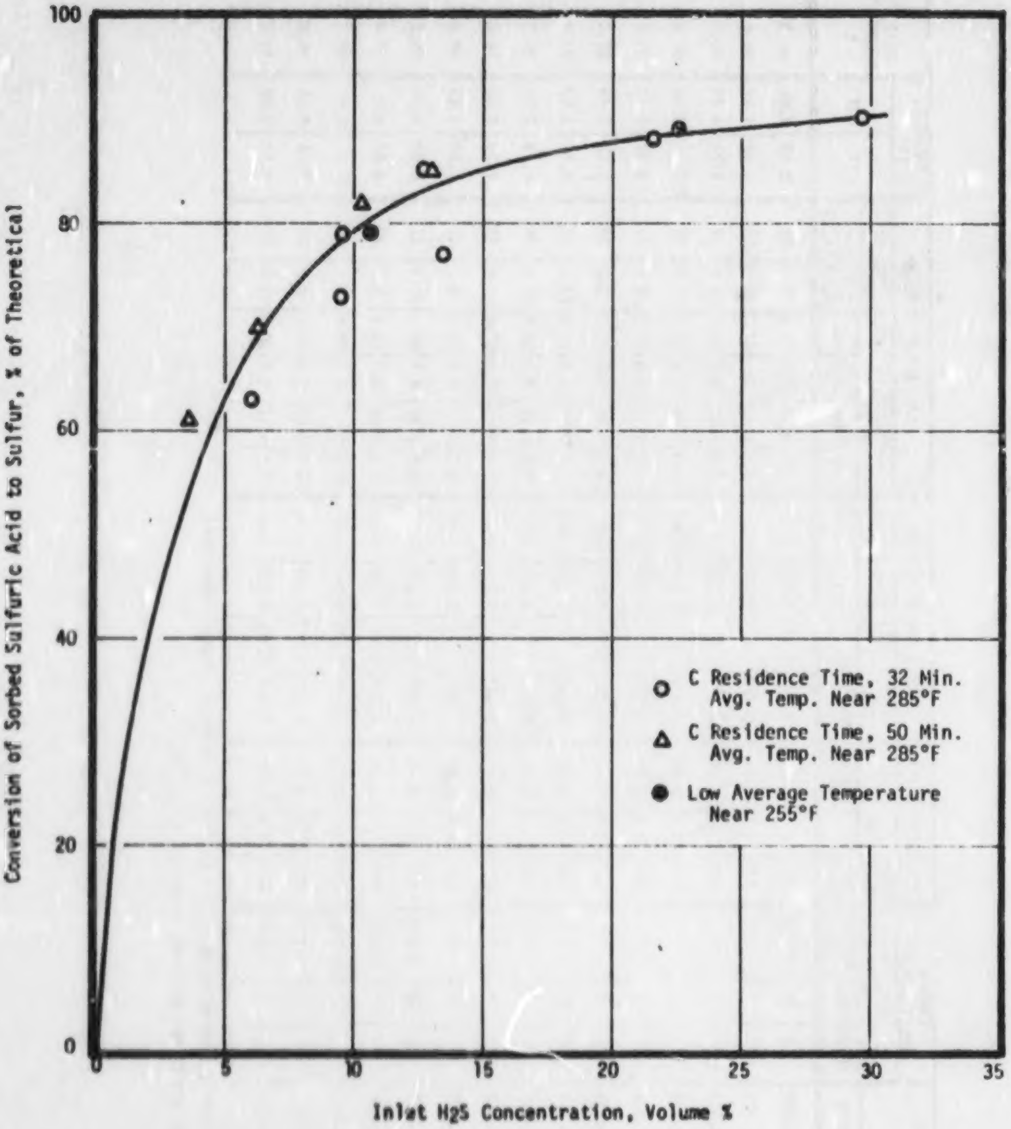
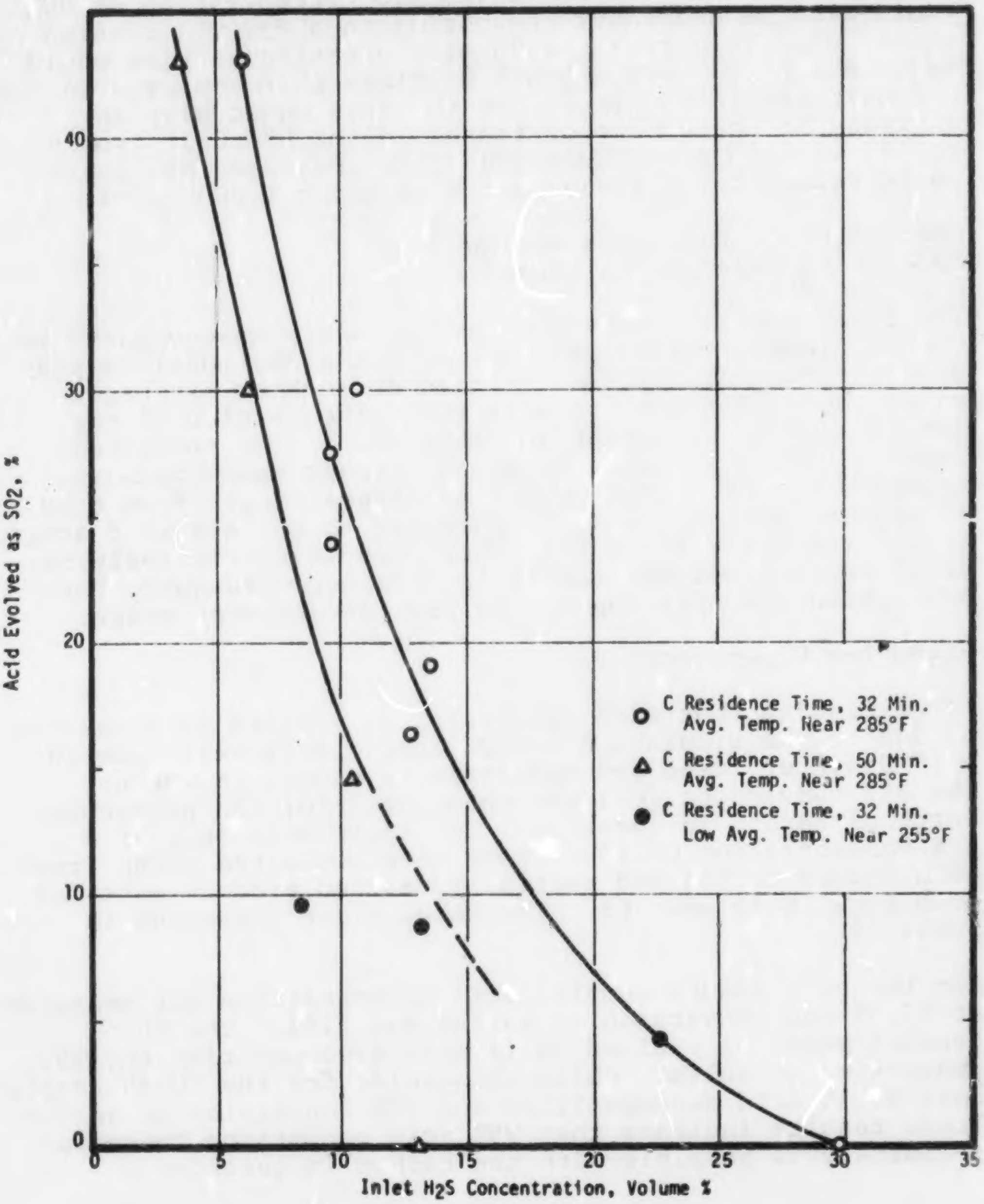


Figure 45. Effect of H_2S concentration and carbon residue time on acid evolved as SO_2 in simulation experiments using a 6" diameter fluid bed unit for integrated operation with an 18" diameter SO_2 sorber



yielded lower acid conversions, in the 60 - 70% range. The results indicated convincingly, therefore, that reactant conversion goals could not be met in the 6" unit. It was estimated based on the experimental data that an increase in carbon residence time in the 6"Ø unit to about 90 minutes would be required to achieve the goal of 99% acid conversion to sulfur. An inlet H_2S concentration of 30% would also be necessary, resulting in a H_2S utilization of about 20%. To obtain the 90 minute residence time would require a carbon bed depth 3.25 times that employed in the 4"Ø unit simulation experiments. This would mean an increase in the number of stages in the 6"Ø unit from 9 to 13, with 8" overflow weirs. The increased bed depth would reduce the space velocity to about 1,000 $hr.^{-1}$.

Comparison of Fluid Bed Design
Model with Experimental Results -

The fluid bed acid converter design model was compared to the 4" diameter fluid bed runs by using the model to predict the theoretical reactor size and number of stages under the conditions for each run. The results of the comparison are presented in Table 28. The predicted reactor volume averages about 30% higher than the actual volume. The predicted number of stages ranges from 8 to 13 with an average of 10.5, compared to the actual 8 stages in the reactor. The model, therefore, conservatively predicts reactor volume, and it is considered adequate for prediction and scale-up to the next development stage.

Fixed Bed Experiments -

After finding that acid conversion is limited to a maximum of 90% in the simulation experiments, tests were made in a 1" diameter fixed bed apparatus to ascertain whether the 99% conversion goal was obtainable for the particular batch of carbon in question. The tests were made at a H_2S concentration of 30%. Runs were conducted using fresh acid loaded carbon and partially reacted product material from Runs SG-65 and -68. The results are presented in Table 29.

For the acid loaded sample, acid decomposition was measured at 97.5% and conversion to sulfur was 119%. The SG-65 product material yielded 98.1% acid decomposition and 99% conversion to sulfur, while the yields for the SG-68 sample were 97.3% acid decomposition and 94% conversion to sulfur. These results indicate that 99% acid conversion to sulfur definitely is possible with the carbon in question.

Table 28. COMPARISON OF THE FLUID BED DESIGN MODEL WITH EXPERIMENTAL SULFUR GENERATION FLUID BED DATA

RUN NO.	AVG. TEMP. °F	CARBON RATE, #/HR.	INLET GAS RATE, CFH @ 70°F	INLET y_{H_2S}	OUTLET y_{H_2S}		INLET ACID LOADING, #/#C		SO_2 EVOL., % INLET ACID	OUTLET ACID LOAD., #/#C	MATERIAL BALANCE, LBS. SULFUR		NUMBER OF STAGES		SPACE VELOCITY, HR.$^{-1}$		TOTAL VOLUME, CU. FT.	
					ACTUAL	CALC.*	ACTUAL	CALC.**			IN	OUT	ACTUAL	CALC.	ACTUAL	CALC.	ACTUAL	CALC.
SG-27	300	42.8	410	0.24	0.100	0.128	0.210	0.210	0	0.1197	11.10	10.30	8	9.5	2,725	2,290	0.1396	0.1663
SG-55	294	9.8	438	0.061	0.016	0.032	0.216	0.125	42.1	0.0150	2.91	2.67	8	12.6	2,850	1,840	0.1396	0.2203
SG-56	294	9.8	436	0.136	0.080	0.092	0.216	0.175	19.2	0.0110	5.61	5.23	8	10.3	2,840	2,250	0.1396	0.1796
SG-57	295	9.8	439	0.096	0.044	0.057	0.216	0.159	26.2	0.0120	4.18	3.86	8	11.8	2,860	1,980	0.1396	0.2057
SG-58	286	6.3	438	0.036	0.015	0.017	0.216	0.127	41.1	0.0130	1.75	1.83	8	12.4	2,850	1,880	0.1396	0.2165
SG-59	290	6.3	438	0.063	0.026	0.039	0.216	0.153	29.0	0.0120	2.73	2.35	8	9.8	2,850	2,380	0.1396	0.1704
SG-60	280	6.3	437	0.104	0.050	0.075	0.216	0.186	14.1	0.0130	4.21	3.38	8	8.3	2,840	2,800	0.1396	0.1448
SG-61	284	6.3	435	0.131	0.080	0.096	0.216	0.216	0	0.0120	5.17	4.46	8	8.0	2,830	2,900	0.1396	0.1390
SG-62	291	9.8	435	0.128	0.073	0.082	0.216	0.182	15.9	0.0110	5.31	5.16	8	11.1	2,830	2,080	0.1396	0.1937
SG-64	286	9.9	439	0.096	0.045	0.055	0.216	0.165	23.6	0.0110	4.18	4.03	8	12.8	2,860	1,820	0.1396	0.2240
SG-65	253	9.8	435	0.134	0.080	0.086	0.216	0.198	8.5	0.0170	5.52	5.35	8	12.2	2,830	1,900	0.1396	0.2123
SG-66	280	9.8	464	0.107	0.048	0.073	0.200	0.144	28.2	0.0090	4.76	4.11	8	11.7	3,020	2,110	0.1396	0.2045
SG-67	289	9.8	443	0.217	0.152	0.166	0.209	0.198	5.0	0.0050	8.64	8.08	8	9.9	2,880	2,370	0.1396	0.1735
SG-68	299	9.8	435	0.298	0.220	0.245	0.208	0.208	0	0.0080	11.4	10.50	8	7.9	2,830	2,940	0.1396	0.1372
SG-69	260	9.8	456	0.226	0.153	0.178	0.207	0.199	4.1	0.0100	9.21	8.30	8	9.7	2,970	2,490	0.1396	0.1698

*Higher outlet H_2S concentration used by computer to obtain correct material balance.

**Inlet acid loading corrected for SO_2 evolution.

Table 29. FIXED BED SULFUR GENERATION EXPERIMENTS

Run Number	Gas Flow cc/min.		Average Temp. °F	Space Velocity hr.$^{-1}$	Carbon Analyses						Acid Decomposition %	Conversion to Sulfur %
					Inlet				Outlet			
						Acid Load, # acid/# C						
	N_2	H_2S			% S	From % S	SO_2 Anal.	Acid Titr.	# S/# C*	# acid/# C		
2	125	55	286	1,000	5.56	0.194**	0.218	0.181	0.30	0.005	97.5	119
3***	"	"	285	"	18.1	---	---	0.020	0.28	0.004	98.1	99
4****	"	"	289	"	0.56	---	---	0	0.016	0.001	---	---
5*****	"	"	282	"	19.3	---	---	0.011	0.25	0.006	97.3	94

*Less residual sulfur on virgin carbon.

**Used as inlet acid loading, since have standard for total sulfur analysis.

***Feed sample to fixed bed from product of Run SG-65 (18.1% S, 0.0164 lb. acid/lb. material).

****Feed is virgin carbon.

*****Feed sample to fixed bed from product of Run SG-68 (19.3% S, 0.00882 lb. acid/lb. material).

The 119% conversion to sulfur for the acid loaded sample was an indication of a separate phenomenon, believed to be reaction of H_2S with chemisorbed oxygen. This would cause additional formation of elemental sulfur on the carbon. To investigate this possibility, a sample of virgin carbon was tested in the fixed bed apparatus, and the results showed enough sulfur formation to account for 7% of the 19% excess conversion. This was considered valid qualitative evidence that reaction of H_2S with chemisorbed oxygen does occur. The other 12% was attributed to experimental and analytical errors.

Development of Moving Bed Reactor for Integrated Pilot Plant

The results of the simulation experiments in the 4" diameter fluid bed reactor indicated that the 6" diameter unit was unsuitable for use as a sulfur generator in the integrated pilot plant because it was oversized for the application. A sulfur generator properly sized to match the existing 18" diameter SO_2 sorber would be only 2.5" diameter, which would not be feasible from a mechanical standpoint.

Fixed bed tests showed that the desired degree of acid conversion was obtainable. This led to the suggestion of a moving bed reactor as an attractive alternative for the fluid bed reactor initially intended for the pilot plant. Exploratory experiments were then carried out in a 1.5" diameter moving bed reactor in order to evaluate the potential of this approach. The results were favorable, indicating acid conversion of 98-100% and H_2S utilization over 99%, at space velocities in the 100 - 330 $hr.^{-1}$ range and carbon residence times between 70 and 185 minutes. The conditions and results of the moving bed runs are compared to fluid bed data in Tables 30 and 31.

The success of the 1.5" diameter moving bed experiments led to the decision to proceed with development of a pilot scale moving bed sulfur generator. Design calculations were made for reactors of 6" and 8" diameters. The 8" diameter size was chosen because in a 6" diameter unit there was a possibility that the minimum fluidizing velocity could be approached in the reactor and seal leg. (A moving bed of this size does not have the fluidization requirements, but in fact fluidization should be avoided.) The design specifications for the 8" diameter moving bed sulfur generator are given in Table 32, and a drawing of the reactor system is shown in Figure 46. Although the overall reactor length is 10 feet, the carbon bed depth is 6 feet in the

TABLE 30. COMPARISON OF FLUID BED AND MOVING BED SULFUR GENERATION TESTS

Equipment	Run No.	Column Temp., °F		Carbon			Hydrogen Sulfide				Acid Lost as SO_2 in Off Gas		Acid Decomp. %	Sulfur Balance In/Out	Outlet Sulfur Load, # S/# C		% Conversion to Sulfur	Space Veloc. hr.$^{-1}$
		Avg.	Range	Inlet Acid Loading # Acid/# C	Residence Time minutes	Rate #/hr.	Conc. %	Stoich. Ratio	Outlet %	Util. %	% Inlet	Conc. in Gas %			Theor.	Actual		
4" Dia. Fluid Bed	SG-68	290	242-320	0.208	32	12.1	29.8	5.1	22.0	26	0	~0	96	1.1	0.271	0.248	90	2,850
Fluid Bed* Modified 6" Dia.		290		0.184	~90	35	30	5	24	~20	0	0	98	---	0.240	0.238	99	1,000
Moving Bed**	SG-73	286	270-300	0.165	~180	1.1	32.3	1.1	~0	>90	0	~0	94	---	0.212	0.216	102	100

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*These are projected results in 6" diameter unit if modified based on all results to operate at a space velocity of 1,000 hr.$^{-1}$, i.e. increase number of stages from 9 to 13 and bed height to 8 inches.

**Actual moving bed data.

Table 31. DATA SUMMARY - 1-1/2" DIAMETER MOVING BED SULFUR GENERATION TESTS

Run No.	Column Temp. °F		Carbon Inlet Stream				Gas Inlet Stream				Carbon Outlet Stream		Gas Outlet Stream								S Balance		% Conv. to S	Acid Decomposition Rate, #Acid/#C/min.	Space Veloc. hr.$^{-1}$
			Reac. Inv. # C	Carbon Rate #C/hr.	Res. Time min.	Acid Load #Acid/#C	Gas Flow CFH @ 70°F	H_2S Conc.		Linear Gas Velocity ft./sec.	Sulfur Load lb. S/lb. C		Composition, Vol. % (Dry)						SO_2 Evol. % In. Acid	H_2S Util. % of Inlet	S In lb.	S Out lb.			
	Avg.	Range						Vol. %	Times Stoich.		Theoretical	Actual	H_2S	SO_2	CO_2	CO	H_2O	N_2							
SG-74	270	260 - 280	3.09	1.02	185	0.19	9.14	29.5	1.1	0.3	0.248	0.248	~0	~0	---	---	N.D.	N.D.	0	>99	0.28	0.27	100	1x10^{-3}	100
SG-79	268	255 - 280	0.92	0.81	68	0.19	6.2	30.6	1.1	0.2	0.252	0.247	.18	.10	---	---	N.D.	N.D.	<1%	>99	0.22	0.18	98	3x10^{-3}	335

Table 32. DESIGN CONDITIONS - MOVING BED SULFUR GENERATOR

Unit Size	
Nominal, NPS	8
I.D., inches	8.33
Temperature, °F	300
Carbon Rate, lbs./hr.	27.7
Acid Load, lb./hr.	0.184
Gas Rate, SCFH	220
Gas Velocity, ft./sec. at 300°F	0.25
Carbon Residence Time at $S = 100$ hr.$^{-1}$, hrs.	2.85
Carbon Inventory at $S = 100$ hr.$^{-1}$, lbs.	79
Carbon Bed Height, ft.	
$S = 100$ hr.$^{-1}$	6
$S = 200$ hr.$^{-1}$	3
$S = 500$ hr.$^{-1}$	1.2
Pressure Drop* at $S = 100$ hr.$^{-1}$, in. H_2O	31
Reactor Length, ft.	10
Seal Leg Length, ft.	
Total Length	8
Purged Length	6
Seal Leg Velocity, ft./sec.	
$S = 100$ hr.$^{-1}$	0.25
$S = 200$ hr.$^{-1}$	<.1
$S = 500$ hr.$^{-1}$	<.1

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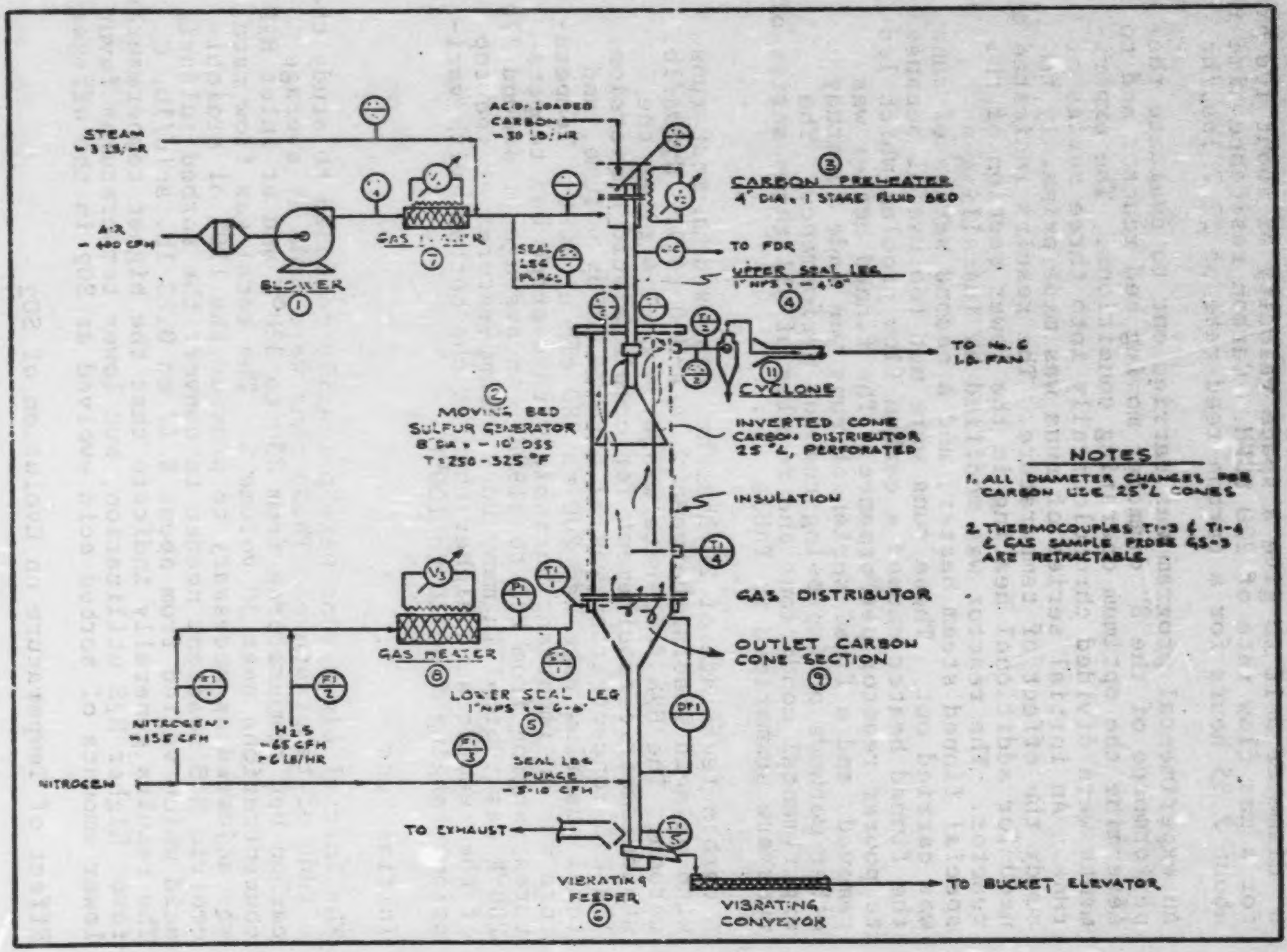
*Based on previously measured pressure drop.

Figure 46. Moving bed sulfur generator


STEAM
~3 LB/HR
AIR
~400 CFM
BLOWER
①
GAS HEATER
⑦
ACID LOADED
CARBON
~30 LB/HR
SEAL
LEG
PURGE
③
CARBON PREHEATER
4" DIA., 1 STAGE FLUID BED
TO FDR
UPPER SEAL LEG
1" NPS × ~4'-0"
④
TO No. 6
I.D. FAN
⑪
CYCLONE
②
MOVING BED
SULFUR GENERATOR
8" DIA. × ~10' OSS
T=250-325 °F
INVERTED CONE
CARBON DISTRIBUTOR
25°L, PERFORATED
INSULATION
GAS DISTRIBUTOR
OUTLET CARBON
CONE SECTION
⑨
GAS HEATER
⑧
LOWER SEAL LEG
1" NPS × ~6'-6"
⑤
NITROGEN
~15E CFH
H₂S
~65 CFH
~6 LB/HR
NITROGEN
SEAL LEG
PURGE
~5-10 CFH
TO EXHAUST
VIBRATING
FEEDER
⑥
VIBRATING
CONVEYOR
TO BUCKET ELEVATOR
NOTES
1. ALL DIAMETER CHANGES FOR CARBON USE 25°L CONES
2. THERMOCOUPLES TI-3 & TI-4 & GAS SAMPLE PROBE GS-3 ARE RETRACTABLE

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8" diameter unit to give a space velocity of about 100 $hr.^{-1}$ for a gas flow rate of 220 SCFH. Carbon residence time is about 2.85 hours for a carbon feed rate of 27.7 lbs./hr.

An experimental program was carried out to evaluate the performnace of the 8" diameter moving bed reactor and to determine the optimum operating conditions. The experiments were divided chronologically into three series of runs. An initial series of runs was made primarily to study the effect of temperature. The results indicated a need for additional heating in the lower section of the reactor. The reactor was modified by installing a special finned steam heater, and a second series of runs was carried out. These runs were not too useful because the finned heater caused a carbon flow problem which led to poorer reactor performance. The finned heater was removed, and a final series of runs was made to study other methods of improving reactor performance. The experimental conditions and results of all three series of runs are summarized in Table 33.

A carbon feed rate of 28 lbs./hr. was used in most runs, with an acid loading between 0.14 and 0.24 lb. H_2SO_4/lb. carbon. The H_2S feed rate was 0.94 to 1.4 times the stoichiometric requirement for complete acid conversion. The H_2S concentration was 27.6 to 34.6% by volume, and total gas flow rate was 200 to 280 cfh at 70°F. Temperature was an important variable with average bed temperatures ranging from 233 to 319°F. An average of around 270-280°F was typical in many runs. Temperatures at the top of the reactor were higher than at the bottom, with variations ranging from 20 to 100°F.

Initial Runs -

The initial eight runs were primarily intended to study the effect of temperature. These runs were made at average carbon bed temperatures from 230 to 320°F and at inlet H_2S concentrations near 30 volume %. The total gas flow rate was adjusted as necessary to provide the 110% of stoichiometric H_2S reactant needed to convert the sorbed sulfuric acid which varied from about 0.17 to 0.23 lb. acid/lb. C. The results generally indicate that the higher temperatures favor higher H_2S utilization, but lower temperatures favor lower amounts of sorbed acid evolved as SO_2 in the off-gas.

Effect of Temperature on Evolution of SO_2 -

The effect of the inlet carbon temperature, which is the maximum measured carbon temperature in the present experi-

Table 33. SUMMARY OF SULFUR GENERATION RESULTS

RUN NO.	COLUMN TEMP., °F		CARBON INLET STREAM				GAS INLET STREAM				CARBON OUTLET STREAM			GAS OUTLET STREAM								SULFUR BALANCE		ACID DECOMP %	CONV TO S %	SPACE VELOC HR.-1	PURPOSE OF RUN
								H2S CONC.**				SULFUR LOADING, #S/#C		COMPOSITION, VOL. %													
	AVG	RANGE	REAC INV. # C	C RATE #C/HR	RES. TIME MIN.	ACID LOAD. #ACID/ #C	* GAS FLOW CFH@ 70°F	VOL. %	TIMES STOICH	LINEAR GAS VELOC. FT/SEC	ACID LOAD. #ACID/ #C	THEO.	ACT.	H_2S	SO_2	CO_2	CO	H_2O	N_2	SO_2 EVOL. % OF INLET ACID	H_2S UTIL. % OF INLET	IN # S	OUT # S				
SG-86	319	305-326	75	28	162	0.167	204	30.5	1.1	0.24	0.019	0.218	0.204	1.2	2.2	0.3	0	37	61.5	27	95	6.9	6.5	88	90	90	Effect of Temp. - 320°F
SG-87	290	260-305	=	28	162	0.185	=	28.8	0.94	0.23	0.023	0.241	0.221	1.6	0.8	0.18	0	35.5	61.6	6	97	6.7	7.0	88	92 ***	90	Effect of Temp. - 290°F
SG-88	253	239-265	=	27	166	0.176	=	27.6	0.96	0.22	0.015	0.239	0.205	5.9	0.09	0.09	0	34.8	62.2	1	74	6.3	7.0	91	90	90	Effect of Temp. - 250°F
SG-88R	262	236-301	=	28	162	0.227	280	30.4	1.1	0.30	0.018	0.296	0.273	2.0	0.90	0.0	0	39.4	56.8	12	92	9.3	8.9	92	92	123	C Prehtr. @320°F & 10%R.H.
SG-89	243	206-296	=	28	162	0.204	280	32.0	1.3	0.30	0.010	0.268	0.264	4.3	0.8	0.1	0	37.1	57.0	12	84	9.7	9.4	95	99	123	C Prentr. @ 280°F & 5%R.H.
SG-90	242	198-300	=	28	162	0.227	280	29.5	1.1	0.30	0.007	0.296	0.285	1.3	0.80	0.0	0	34.8	59.7	10	95	9.0	8.5	97	94	123	C Prehtr. @ 300°F & 5%R.H.
SG-91	233	192-236	=	28	162	0.220	280	31.8	1.2	0.29	0.012	0.287	0.281	4.7	0.43	0.09	0	38.1	59.3	6	82	9.8	9.7	94	98	123	C Prehtr. @ 280°F & 10%R.H.
SG-92	244	203-289	=	28	162	0.212	280	32.1	1.3	0.30	0.007	0.277	0.284	3.5	0.61	0.09	0	40.6	59.8	11	83	9.8	9.6	97	102	123	C Prehtr. @ 280°F & 10%R.H.; Add'l htg from Wall at Bottom of Reactor

*From rotameters

**As determined by gas chromatograph.

***An error analysis indicated the maximum uncertainty in this number is ±10%. The error in the sulfur material balance was calculated to be ±0.3 for inlet # S in.

(continued)

Table 33 (continued). SUMMARY OF SULFUR GENERATION RESULTS

RUN NO.	COLUMN TEMP., °F		CARBON INLET STREAM				GAS INLET STREAM				CARBON OUTLET STREAM			GAS OUTLET STREAM								SULFUR BALANCE		ACID DECOMP %	CONV TO S %	SPACE VELOC HR.$^{-1}$	PURPOSE OF RUN
								H_2S CONC.**				SULFUR LOADING, #S/#C		COMPOSITION, VOL. %													
	AVG	RANGE	REAC INV. # C	C RATE #C/HR	RES. TIME MIN.	ACID LOAD. #ACID/#C	* GAS FLOW CFH @ 70°F	VOL. %	TIMES STOICH	LINEAR GAS VELOC. FT/SEC	ACID LOAD. #ACID/#C	THEO.	ACT.	H_2S	SO_2	CO_2	CO	H_2O	N_2	SO_2 EVOL. % OF INLET ACID	H_2S UTIL. % OF INLET	IN # S	OUT # S				
SG-94	280	250-305	70	28	151	0.239	214	32.4	1.0	0.25	0.046	0.287	0.226	3.0	0.95	0.12	0	37.4	56.0	10	89	8.8	8.1	81	74	100	Dir. 18" to 8"
SG-95	283	247-312	-	24	176	0.229	231	34.6	1.3	0.27	0.039	0.299	0.251	5.5	1.02	0.07	0	36.3	54.6	14	82	9.1	8.3	83	84	110	Dir. 18" to 8" (Higher H_2S Stoich. Ratio)
SG-93	279	238-310	-	24	176	0.224	214	32.6	1.3	0.25	0.047	0.293	0.227	7.0	0.37	0.08	0	34.6	53.5	5	80	8.6	7.7	79	77	100	C Prehtr. @ 260°F & 10% R.H.
SG-96	276	237-311	-	24	175	0.222	214	32.2	1.3	0.25	0.052	0.290	0.221	7.2	0.31	0.07	0	33.7	52.7	4	74	8.7	8.0	77	76	100	C Prehtr. @ 270°F & 10% R.H.
SG-99	274	254-285	75	28	162	0.163	206	32.8	1.3	0.26	0.007	0.212	0.194	4.4	0.35	0	0	36.3	59.1	5	85	7.5	6.7	96	92	90	C Prehtr. @ 270°F & 10% R.H.
SG-100	282	266-299	-	28	162	0.166	206	33.0	1.3	0.26	0.009	0.217	0.200	5.0	0.38	0	0	36.6	59.0	5	83	7.5	6.9	95	92	90	Increas. C Temp. with Inlet Gas
SG-101	277	259-292	-	28	162	0.168	206	33.0	1.3	0.26	0.007	0.220	0.202	5.4	0.33	0	0	34.1	59.2	4	81	7.6	7.1	96	92	90	Increas. C Temp. with C Precond.
SG-103	255	251-273	-	28	162	0.143	200	31.0	1.4	0.25	0.011	0.187	0.199	4.0	0.22	0	0	36.2	59.8	3	85	6.9	6.7	92	106	90	Decreas. H_2S Conc
SG-102		280-316	-	28	162	0.227	206	32.9	1.0	0.26	0.014	0.296	0.190	4.1	1.34	0	0	33.9	60.7	13	86	8.0	6.8	94	64	90	Dir. 18" to 5"; Moisture Level

*From rotameters

**As determined by gas chromatograph.

in Figure 47. As can be seen, as the inlet carbon temperature was decreased from 325 to 265°F, the evolution of SO_2 decreased from about 30% to 1% of the inlet acid. The data indicates that the "best" temperature for the inlet carbon would be in the range of 250 to 270°F.

Effect of Temperature on H_2S Utilization -

The effect of the inlet carbon temperature (maximum reactor temperature) on the utilization of H_2S is given in Figure 48. The data indicate that as the temperature increased from 260°F to 325°F, H_2S utilization increased from 75% to 97%. The condition favoring highest H_2S utilization is the higher reactor temperature.

Effect of Temperature on Per Cent Conversion to Sulfur -

The effect of the inlet carbon temperature on the per cent conversion to sulfur is shown in Figure 49. As can be seen the percent conversion passes through a maximum at about 285 to 295°F due to a decreased acid evolution as SO_2 and then decreases after 285°F because of a decreased utilization of H_2S.

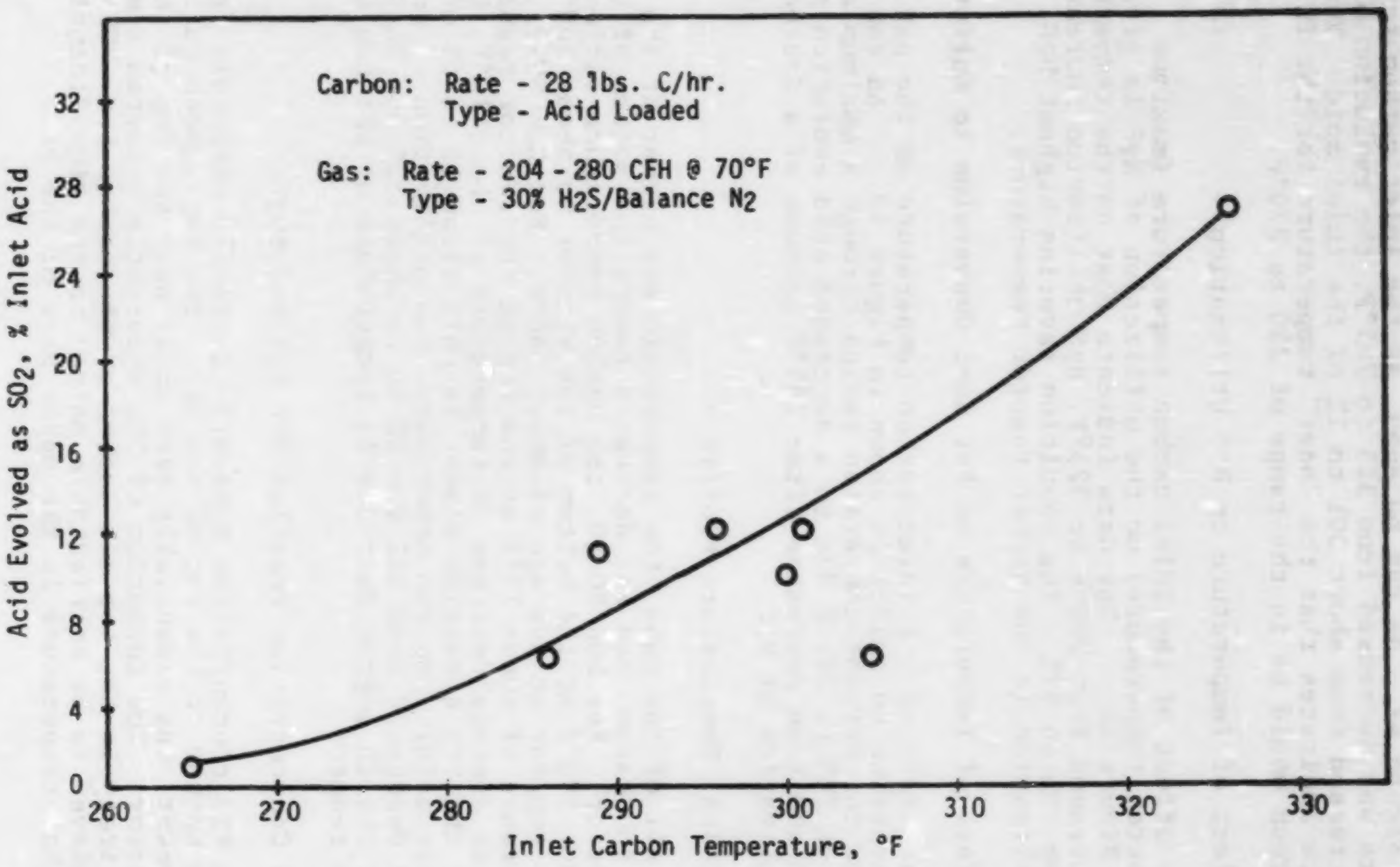
Vertical Temperature Profile -

In all of the runs, the temperature was higher at the top of the carbon bed and decreased toward the bottom of the reactor. For Run SG-90, the carbon temperature varied from about 190°F at the bottom of the reactor to about 300°F at the top, for an average of about 240°F. For Run SG-91, a decrease of about 15°F at the top of the reactor resulted in an average decrease in temperature of about 10°F, but cut the SO_2 evolution almost in half (from 10 to 6% of inlet acid). On the other hand, the utilization of inlet H_2S decreased from 95% for SG-90 to about 82% for SG-91 for the 15 degree decrease in temperature at the top of the reactor.

Gas Concentration Profiles for H_2S and SO_2 -

The H_2S concentration typically decreased uniformly from the bottom to the top of the bed. The SO_2 concentration, however, was essentially zero until near the top of the reactor. The formation of SO_2 apparently occurred almost entirely in the top six inches of the carbon bed. This is believed to be attributable mainly to the significantly higher temperature in the upper part of the bed.

Figure 47. Effect of inlet carbon temperature* on the evolution of H_2SO_4 as SO_2 in an 8" diameter moving bed reactor



*Also maximum temperature in the present experiments.

Figure 48. Effect of inlet carbon temperature on H2S utilization in an 8" diameter moving bed reactor

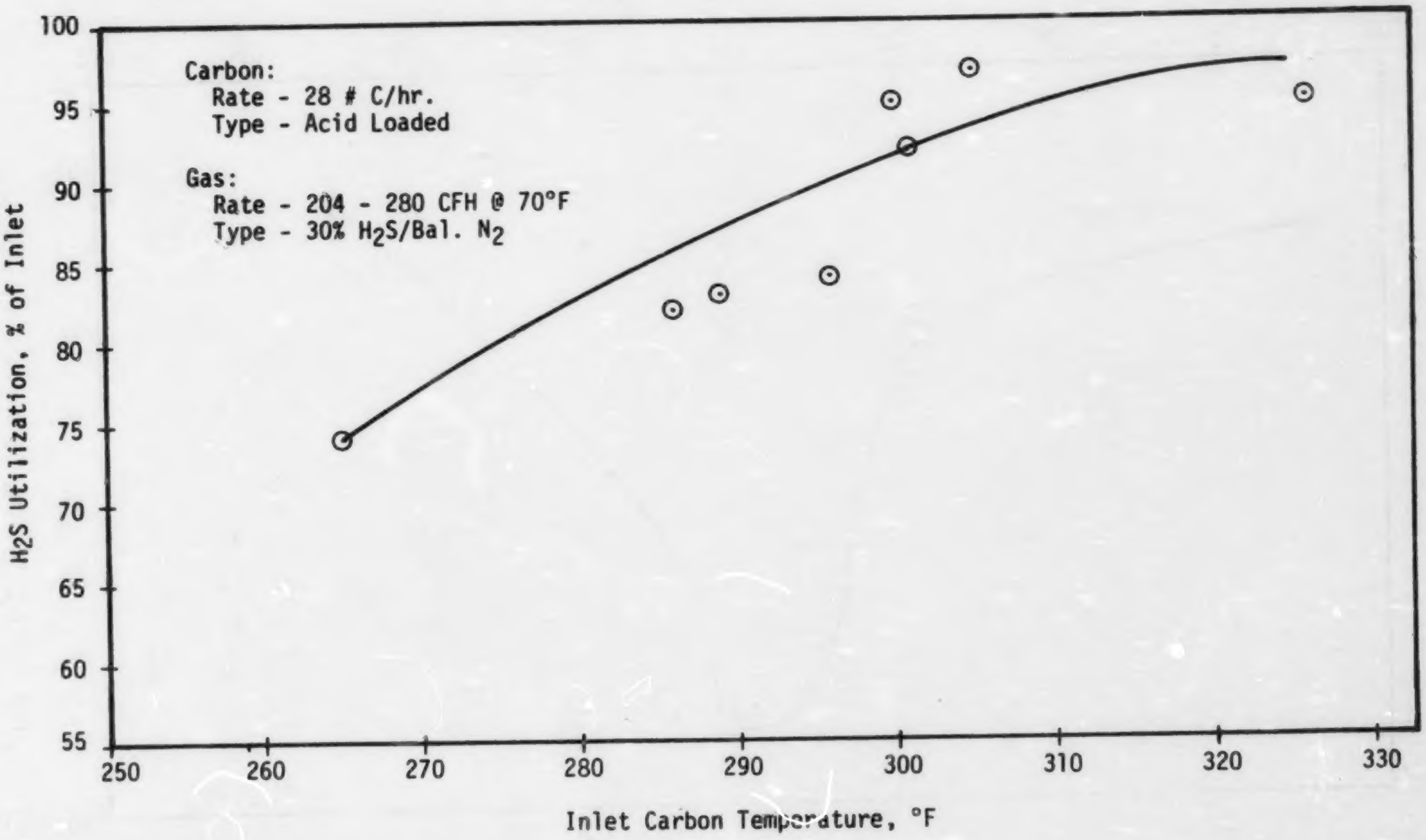
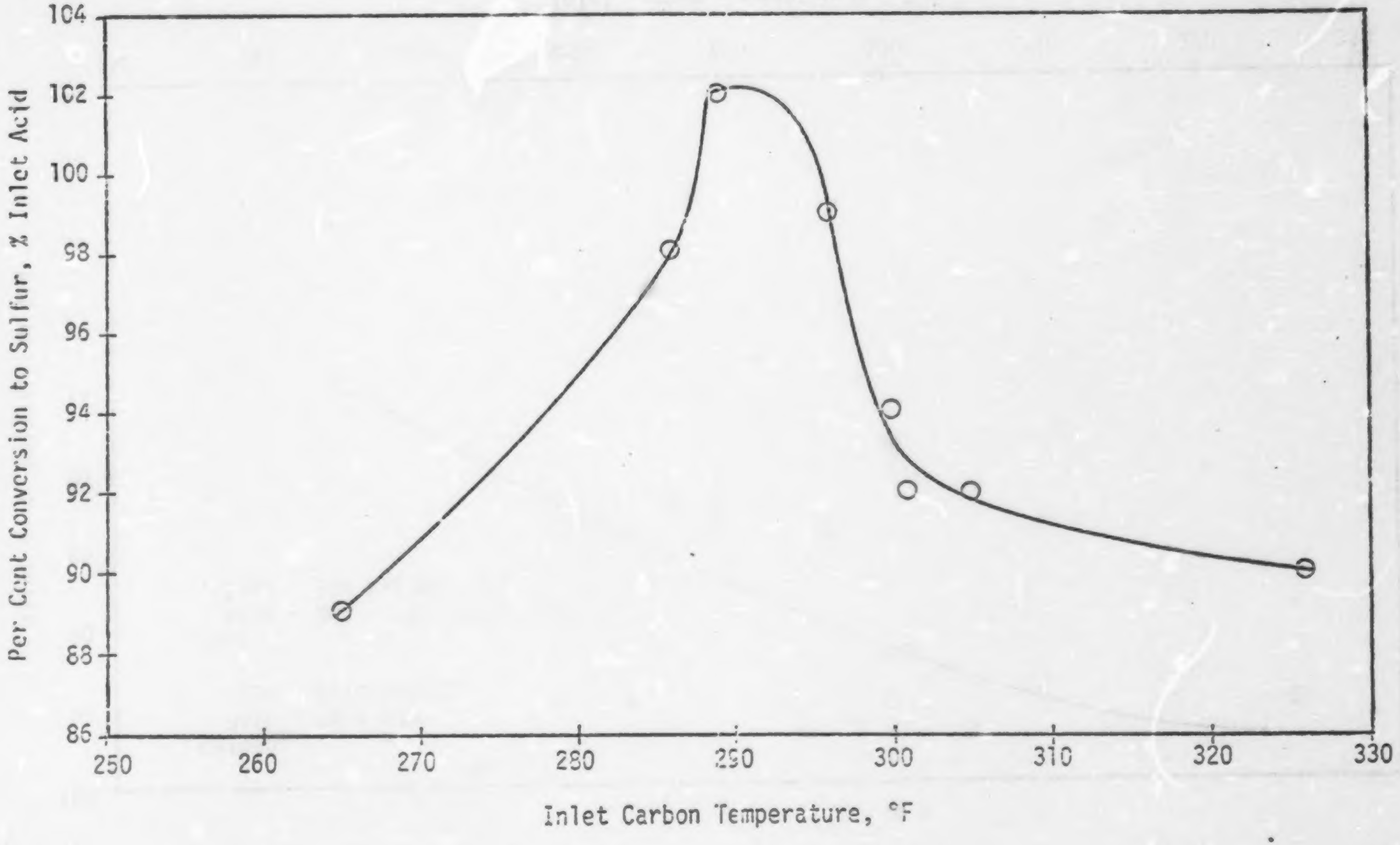


Figure 49. Effect of the inlet carbon temperature on the per cent conversion to sulfur



Strategy for Improving Performance of 8" Diameter Moving Bed -

The results of the initial eight runs indicated that a substantial improvement in performance could be obtained if the vertical temperature profile was modified so as to raise the temperature in the bottom of the reactor and lower it at the top. The anticipated effects were a reduction in formation of SO_2 and an increase in H_2S utilization. Modifying the temperature profile in this way required some means of providing additional heat input to the bed. To obtain this heat, a finned steam-operated heat exchanger was installed vertically inside the reactor.

Finned Steam Heater Experiments -

A series of four runs, SG-93, -94, -95 and -96, was made with the finned steam heater installed. The finned heater was successful in raising the temperature, as shown in Figure 50. Reactor performance did not improve, however, due to carbon flow stagnation on one side of the reactor, which was caused by the presence of the heater. A residence time distribution study clearly showed flow stagnation and a large deviation from plug flow. This is shown in Figure 51.

In these runs the 18" diameter SO_2 sorber was run concurrently with the 8" diameter moving bed acid converter. The four runs included two runs with the carbon from the sorber routed directly to the 8" diameter unit, and two runs with the carbon passing from the sorber to the 6" diameter carbon conditioner and then into the 8" diameter moving bed.

As seen in Table 33, the results of these runs are significantly poorer than the results of the first series of runs. The H_2S utilization is consistently less than 90% and acid conversion to sulfur averages only 80%. Formation of SO_2 is about the same as before. Further discussion of the results would not be meaningful in view of the overall performance reduction which resulted from installation of the finned heater.

Final Series of Runs -

After determining that the flow problem associated with the finned heater could not be corrected, the heater was removed and a final series of runs was made. The objective in these runs was to study the effects of 1) additional heat input from sources other than an internal heat exchanger, 2) H_2S concentration, and 3) moisture content of the entering carbon.

Figure 50. Effect of steam heater on improved carbon heating capabilities

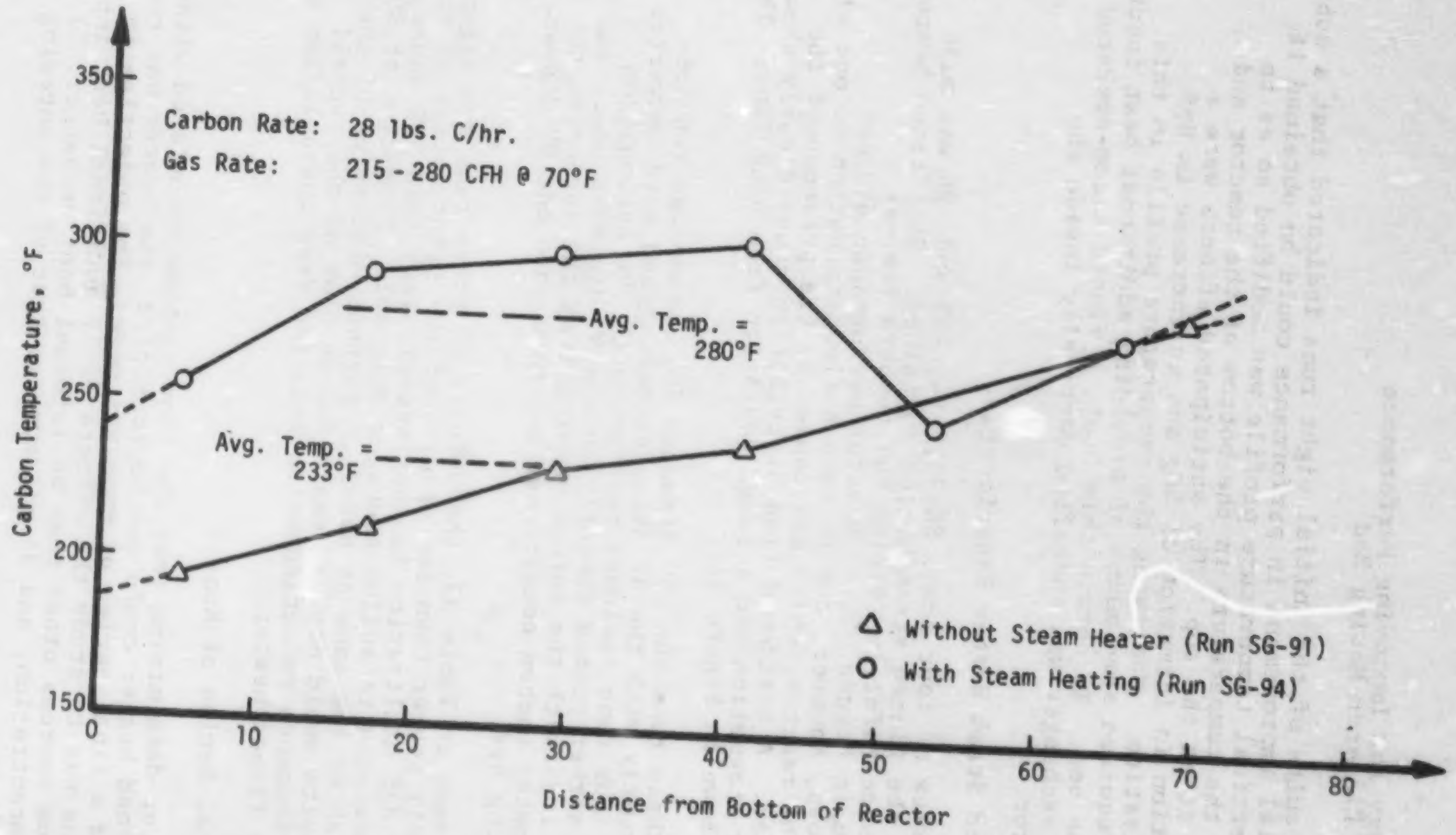
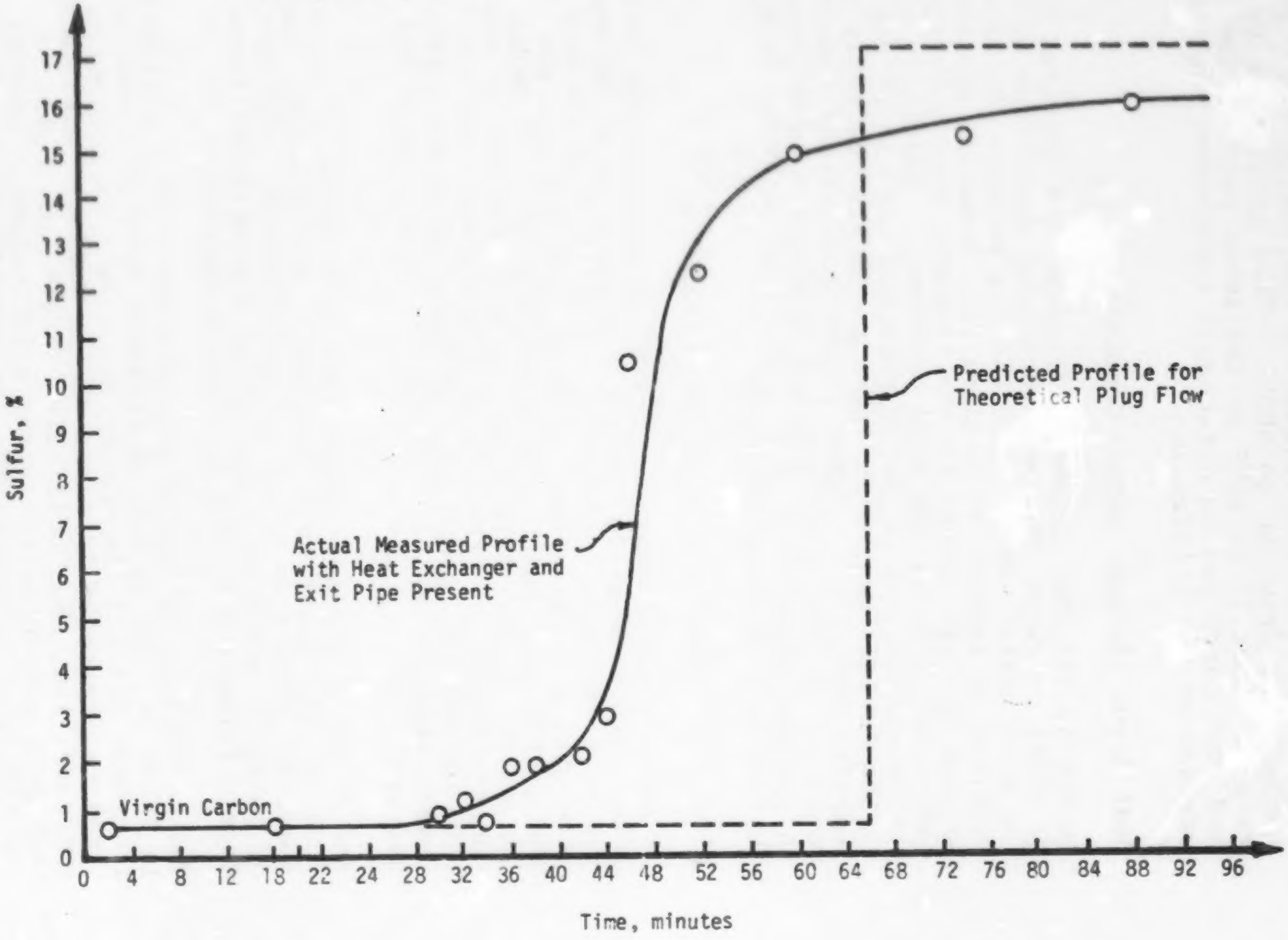


Figure 51. Effect of heat exchanger system (1-1/2" pipe x 4") on carbon flow in an 8" diameter moving bed reactor - tracer feed composition



Heat Input through Inlet Gas -

In Run SG-100, an attempt was made to raise the temperature in the bottom of the reactor by increasing the inlet gas temperature from 300 to 400°F. This produced a temperature rise of about 10 to 20°F in the lower part of the carbon bed, but there was no noticeable improvement in acid conversion or H_2S utilization.

Heat Input through Carbon Conditioner -

In Run SG-101, the carbon conditioner was operated at 325°F in order to raise the temperature of the carbon entering the 8" diameter unit. This did not produce the expected increase in carbon bed temperature, however, apparently because of heat losses in the transfer piping between the carbon conditioner and acid converter. Operating the carbon conditioner at 325°F required the use of pure steam as the fluidizing gas in order to obtain the desired 15% relative humidity. Higher carbon conditioner temperatures would not be practical because it would then be necessary to operate above atmospheric pressure in order to obtain the desired relative humidity.

Effect of Inlet Carbon Moisture Content -

In all the experiments in the 8" diameter moving bed, the inlet carbon moisture content was found to be an important parameter in acid conversion. Variation of the moisture level had a large effect on the temperature at the top of the carbon bed, which apparently was directly related to the extent of SO_2 formation. At a low moisture level, the temperature at the top of the bed was high and formation of SO_2 was also high. By increasing the moisture level, temperature was lowered and formation of SO_2 was reduced.

The probable explanation is that adsorption of water vapor from the gas phase onto the carbon occurs unless the carbon moisture content is above a certain level. Adsorption of water is exothermic and causes the observed temperature rise. Formation of SO_2 is the end result.

The results in Tables 33 and 34 support this explanation. In Table 34, the carbon conditioner operating conditions are shown for all the moving bed runs. Carbon moisture level is presented in terms of the sulfuric acid solution concentration, lbs. acid/(lbs. acid + lbs. H_2O). A high acid concentration means a low moisture content. The effect of moisture level on temperature in the top of the bed and on SO_2 formation is seen by comparing Runs SG-94 and -95 with Runs SG-100 and -101. These runs are chosen for comparison because the average bed

Table 34. EFFECT OF VOLUME % H2O AND TEMPERATURE ON THE CONCENTRATION OF ACID SOLUTION SORBED ON CARBON FOR CARBON PREHEATER

Run No.	Total Gas Flow Rate, CFH @ 70°F	Steam Conc., Vol. %	Temp., °F	Relative Humidity, %	Acid Conc., # Acid/(# Acid + # H_2O)		
					In	Out	
						Predicted	Meas.
SG-86	1,070	12	310	2.3	---	0.83	---
SG-87	1,070	12	277	3.7	---	0.78	---
SG-88	1,070	12	245	6.5	---	0.74	---
SG-88R	940	46	317	7.9	0.76	0.75	---
SG-89	960	17	276	5.3	0.73	0.76	---
SG-90	920	24	300	5.3	0.79	0.78	---
SG-91	950	34	276	10.8	0.75	0.70	---
SG-92	950	34	283	9.7	0.75	0.72	---
SG-94	---	13*	290	3.3	---	0.80	0.82
SG-95	---	13*	290	3.3	---	0.80	0.79
SG-93	1,010	28	280	8.3	---	0.73	0.73
SG-96	1,070	23	274	7.6	---	0.74	0.74
SG-99	1,153	65	300	14.3	---	0.70	0.71
SG-100	1,169	65	301	14.0	---	0.70	---
SG-101	1,025	100	327	14.9	---	0.70	---
SG-103	1,177	65	296	15.3	---	0.68	0.72
SG-102	---	13*	290	3.3	---	0.80	0.87

*Carbon direct from 18" diameter SO_2 sorber to 8" diameter sulfur generator.

temperatures are all in the 277-283°F range. In SG-94 and -95 the relative humidity in the carbon conditioner was 3.3% compared to about 14.5% in SG-100 and -101. These conditions produced a low moisture level in SG-94 and -95, and a high moisture level in SG-100 and -101. The results in Table 33 show an average SO_2 formation of 12% in SG-94 and -95 compared to 5% in SG-100 and -101, which is a significant difference.

Overall Reactor Performance Summary -

The results of the final moving bed runs showed that performance of the 8" diameter reactor was adequate for the intended application as the acid converter for the integrated pilot plant. Conservatively, the results indicated that the reactor could be expected to perform at the following levels:

Acid Decomposition	>95%
Acid Conversion to Sulfur	>92%
Acid Conversion to SO_2	< 5%
H_2S Utilization	>85%

Although better results for each individual response were obtained in some runs, the above performance levels represent conditions that can be expected with a fair degree of certainty.

Comparison of Moving Bed Runs with Design Model -

Based on the rate expression for the acid decomposition reaction, a design model was derived for a moving bed reactor, assuming plug flow of both the carbon and gas phases. The design model was used to predict reactor volume for the conditions in the moving bed experiments. The results of the comparison are shown in Table 35.

It is seen that the predicted reactor volume in all of the 8" diameter moving bed runs is less than the actual volume by a factor of 6. In view of the possible gas channelling and solids flow problems inherent in the moving bed used, these discrepancies might be expected.

The design model comparison demonstrates, therefore, that the results of the 8" diameter moving bed experiments are unsuitable for purposes of reactor modeling. This had no effect, however, on the adequacy of the 8" diameter moving bed reactor to perform the acid conversion step in the integral pilot plant runs.

Table 35. COMPARISON OF THE MOVING BED DESIGN MODEL WITH EXPERIMENTAL SULFUR GENERATOR MOVING BED DATA

RUN NO.	AVG. TEMP. °F	CARBON RATE, #/HR.	INLET GAS RATE, CFH @ 70°F	INLET y_{H_2S}	OUTLET y_{H_2S}		INLET ACID LOADING, #/#C		SO_2 EVOL., % INLET ACID	OUTLET ACID LOAD., #/#C	MAT'L. BAL., LBS. SULFUR		BED HEIGHT, INCHES		TOTAL VOLUME, CU. FT.	
					ACTUAL	CALC.*	ACTUAL	CALC.**			IN	OUT	ACTUAL	CALC.	ACTUAL	CALC.
SG-74	270	1.02	9.14	0.295	0.0005	0.0565	0.190	0.190	0	0.010	0.286	0.257	82.9	15.46	0.0848	0.0158
SG-79	270	0.81	6.20	0.306	0.0018	0.028	0.190	0.190	0	0.010	0.208	0.204	16.8	13.03	0.0172	0.0133
SG-99	274	28.0	206	0.328	0.044	0.090	0.163	0.155	4.9	0.007	7.092	6.381	72.0	12.39	2.094	0.366
SG-100	282	28.0	206	0.330	0.050	0.091	0.166	0.158	4.8	0.009	7.153	6.683	72.0	11.67	2.094	0.339
SG-101	277	28.0	206	0.330	0.054	0.083	0.168	0.161	4.2	0.007	7.172	6.784	72.0	12.76	2.094	0.371
SG-102	300	28.0	206	0.329	0.041	0.041	0.227	0.198	12.8	0.018	7.694	6.238	72.0	11.54	2.094	0.336
SG-103	265	28.0	200	0.310	0.040	0.098	0.143	0.139	2.8	0.011	6.447	6.432	72.0	11.53	2.094	0.335
INT-7	289	29.0	228	0.272	0.0003	0.039	0.220	0.189	14.1	0.034	7.225	6.719	72.0	11.11	2.094	0.323

*Higher outlet H_2S concentration used by computer to obtain correct material balance.

**Inlet acid loading corrected for SO_2 evolution.

5.2.3 Sulfur Removal

The sulfur sorbed on the activated carbon has to be removed to recover the sulfur values and to regenerate the carbon for reuse. Two basic methods were used to effect this sulfur removal. The first was to vaporize the sulfur from the carbon, and other was to extract the sulfur. The bench scale results of each of these methods are discussed, followed by a comparison of the two methods.

Under thermal sulfur recovery, equilibrium data of sulfur adsorbed on activated carbon is presented. The sulfur stripping runs made in fluid bed reactors are presented, but since it was demonstrated that the unit operations of sulfur stripping and of H_2S generation could be combined into one reactor the operational data on sulfur stripping only is more limited than combined operation discussed in Section 5.2.4 (H_2S Generation).

Sulfur recovery by solvent extraction is also presented.

The two methods of sulfur recovery were compared by recycle experiments of six carbon cycles. The data indicated that sulfur vaporization from carbon was preferred because the SO_2 activity of the carbon was maintained, whereas the solvent extracted carbon required further treatment.

As back-up information, a pilot plant was designed for sulfur recovery from carbon by solvent extraction. The design and economics are presented.

Thermal Stripping Studies -

Equilibrium adsorption data for sulfur vapor on activated carbons were obtained by contacting carbon with a known partial pressure of sulfur in a stream of nitrogen followed by combustion analysis of the carbon to determine sulfur loading.

The sorbed sulfur was assumed to exist in both physically adsorbed and chemisorbed states. The amount chemisorbed was taken as the residual loading after extended purging with inert gas, and assumed to be constant below 1000°F. The remaining physically adsorbed portion was found to be characterized by a form of the Polanyi-Dubinin adsorption equation with respect to equilibrium vapor pressure and temperature:

$$\ln(L - L_c) = A - K\left(T \log \frac{P_s}{P}\right)^2 \qquad (43)$$

where L = total equilibrium sulfur loading
L_c = the amount chemisorbed
T = adsorption temperature
P_s = saturation vapor pressure of sulfur at T
P = equilibrium sulfur pressure
A, K = constants.

Data which fit this equation were obtained over ranges of temperature, pressure, and loading which are of interest in the analysis of thermal stripping operations associated with SO_2 recovery.

A search of the literature shows that previous activities in the field have been primarily concerned with sulfur chemisorption on carbon. An exception is the work of Juza and Blanke[2] who measured sulfur vapor isotherms manometrically under static conditions. Data obtained for two activated carbons showed evidence of chemisorption, physical adsorption, and capillary condensation over various ranges of sulfur loading at temperatures of about 700°F.

In the present work, adsorption measurements were made dynamically rather than under static conditions in order to avoid complications due to the production of gaseous reaction products.

Experimental Results for Equilibrium of Sulfur over Carbon -

Table 36 lists the equilibrium sulfur loadings found on carbon at the various experimental carbon temperatures and sulfur vapor pressures. These pressures were taken from the corresponding sulfur temperatures according to data presented in the SULFUR DATA BOOK[3].

Inspection of Table 36 shows that at the higher sulfur loadings, the amount sorbed depends upon both temperature and vapor pressure as would be expected in physical adsorption. It is seen from the purge data, however, that

Table 36. EXPERIMENTAL RESULTS OF EQUILIBRIUM SULFUR ADSORPTION MEASUREMENTS

Carbon Adsorption Temperature, °F	Sulfur Generator Temperature, °F	Sulfur Vapor Pressure, torr	Equilibrium Sulfur Loading, gms S/100 gms C
Adsorption Data			
650	550	38	63.0
650	450	7.1	47.7
800	550	38	46.6
800	450	7.1	31.8
1000	550	38	24.3
800	380	1.55	16.2
1000	450	7.1	12.7
800	325	0.36	10.6
Purge Data			
1000	---	0	7.3
1200	---	0	7.1
1400	---	0	6.6

there exists at a given temperature a minimum sulfur loading. Figure 52, showing experimental adsorption isotherm points for 1000° and 800°F, illustrates this further. As the equilibrium pressure approaches zero, a residual loading is retained which probably represents chemisorbed material. Attempts to describe equilibrium adsorption of sulfur in terms of sulfur loading, vapor concentration and carbon temperatures must, therefore, consider both physically and chemically bound sulfur.

It has now been found that the temperature dependency of the experimental sulfur sorption data is well represented by a form of the Polanyi-Dubinin adsorption, Equation 43. Figure 53 shows the data of Table 36 plotted in this form as $\ln(L - L_c)$ vs. $(T \log P_s/P)^2$ where L_c was assumed to be constant below 1000°F, the maximum temperature of the equilibrium data. Taking Slope K and intercept A from the straight line plot, the adsorption equation becomes:

$$\ln(L - 7.3) = 4.10 - 0.179\left(T \log \frac{P_s}{P}\right)^2 \times 10^{-6} \qquad (44)$$

where L = gm S/100 gms C
T = °R.

Figure 52. Experimental adsorption isotherm points for sulfur on activated carbon at 800° and 1000°F

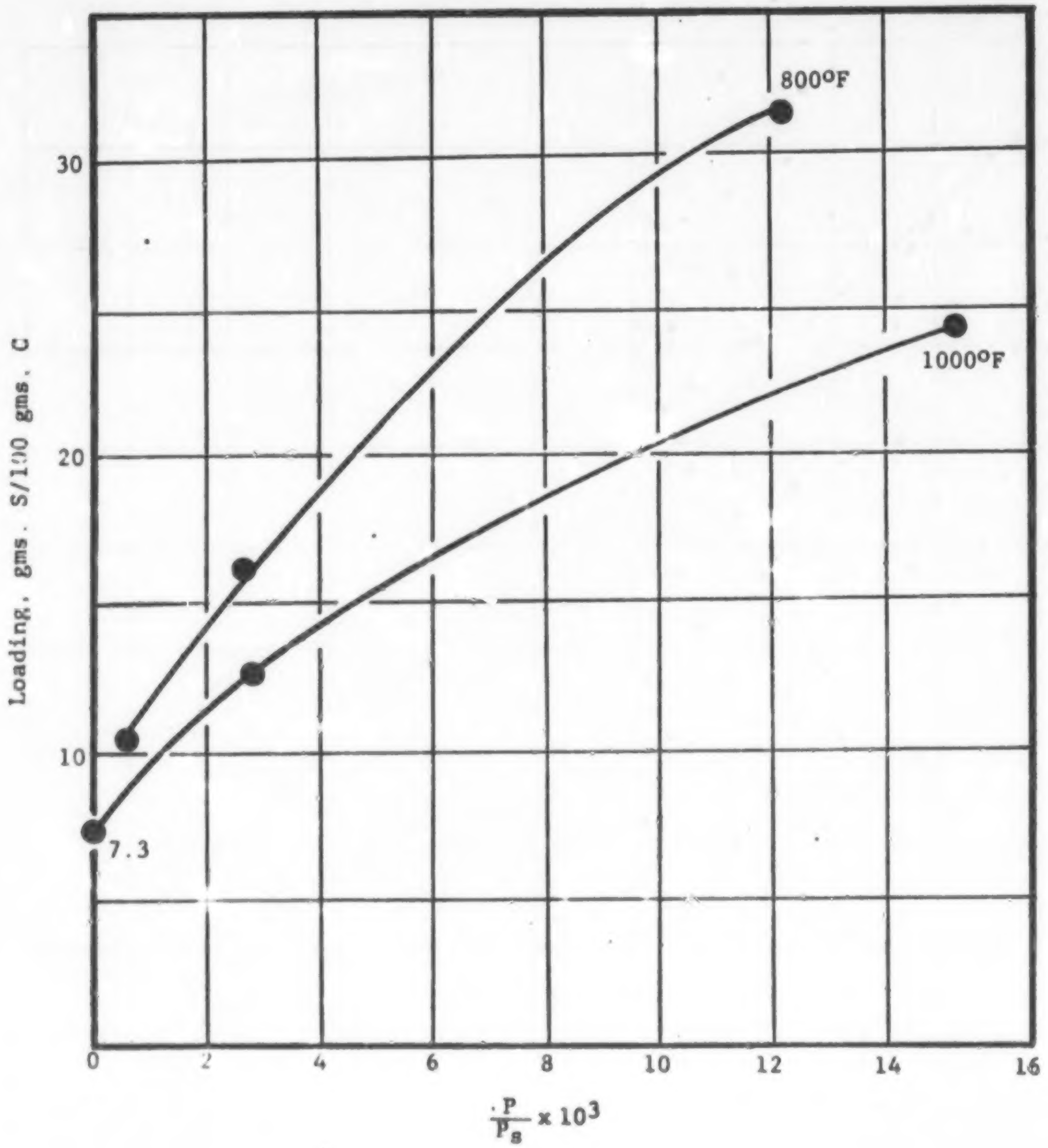
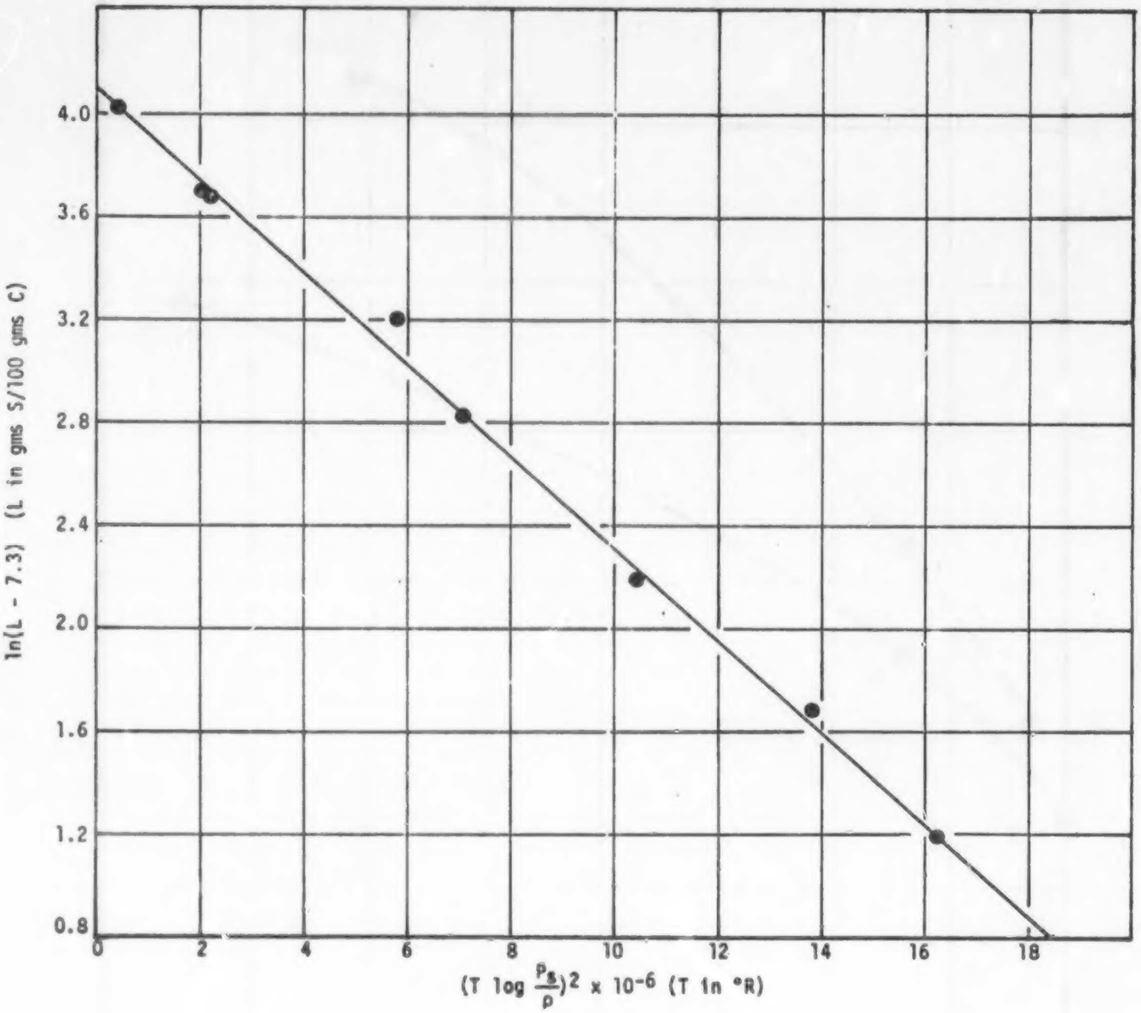


Figure 53. Polanyi-Dubinin plot of sulfur adsorption data



Using this equation the partial pressure of sulfur in equilibrium with carbon having a given loading can be calculated at any temperature up to about 1000°F. At higher temperatures, up to 1400° for example, better results might be obtained by substituting correct values for L_c as determined by extended purging. Such values are noted in Table 36. In this case it would be necessary to recalculate the proper values for constants A and K.

For the purposes of analyzing thermal stripping data, it may be more convenient to express vapor pressures in terms of sulfur concentration. Since sulfur exists in the vapor phase as polyatomic molecules in which molecular weight depends on temperature, the relationship between pressure and concentration is:

$$\% S_1 = \frac{P}{760} \times [\frac{M}{32}]_T \qquad (45)$$

where $\% S$ = concentration expressed as monatomic sulfur at 1 atm. total pressure

P = vapor pressure in torr

$[\frac{M}{32}]_T$ = average number of sulfur atoms per molecule at the temperature of interest.

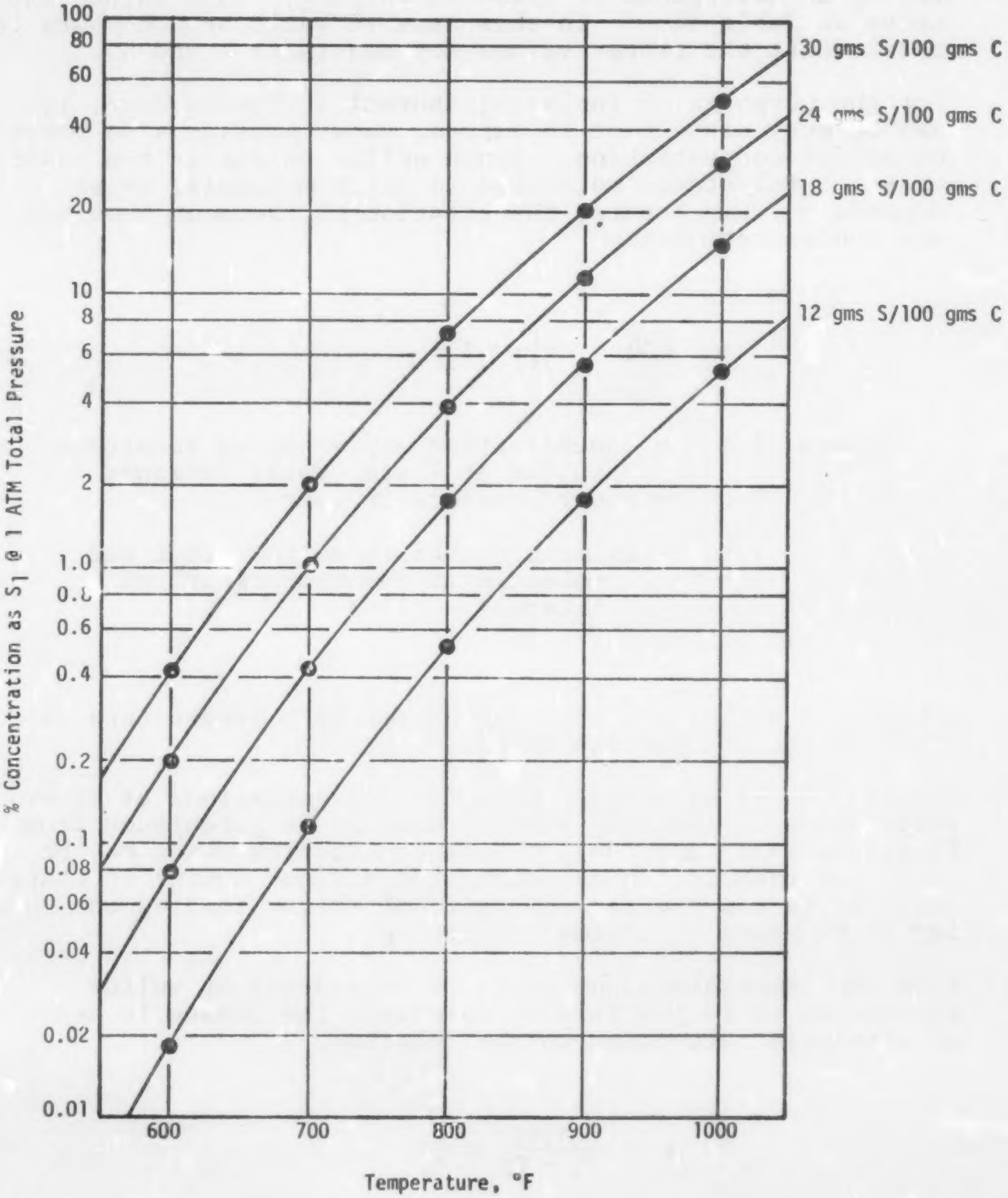
A table of values for this latter term vs. temperature is given in the SULFUR DATA BOOK[3].

Figure 54 shows a plot of sulfur concentrations as S_1 vs. temperature for various sulfur loadings as calculated from Equations (45) and (46). Such equilibrium lines may be used, for example, to calculate the minimum number of stages required to reach a certain residual sulfur loading on carbon by means of thermal stripping.

From the temperature and pressure dependency of sulfur adsorption it is possible to calculate the isosteric heat of adsorption according to the relation:

$$q = \frac{RT_1T_2}{T_1 - T_2} \ln \frac{P_1}{P_2} \qquad (46)$$

Figure 54. Equilibrium lines for concentration vs. temperature at various loadings



where P_1 = equilibrium pressure at temperature T_1
P_2 = pressure at T_2
q = differential heat of adsorption evaluated at a particular loading.

The calculated heats of physical adsorption are given in Table 37 for various total loadings.

Table 37. ISOSTERIC HEATS OF ADSORPTION OF SULFUR VAPOR ON CARBON

Total Load gms S/100 gms C	q Kcal/mol	q BTU/lb.
12	24.7	223
18	23.0	208
24	21.9	198

These heats of adsorption which must be supplied during stripping may be compared to the heat of vaporization of bulk sulfur of 134 BTU/lb. at 1000°F. The relative magnitudes of these heats are reasonable for systems involving physical adsorption.

Comparison of the experimental sulfur adsorption isotherm results obtained here with those of Juza and Blanke noted previously was made by means of Polanyi-Dubinin type plots. Their data obtained near 700°F showed similarities to the present data within the limits which might be expected to result from variations in carbon type. However, the temperature dependency was not properly described by the P-D relation since the few data reported for higher temperatures did not fall on a single curve with those at 700°F. The reason for disagreement is not clear although it is possible that small amounts of gaseous reaction products formed at the higher temperatures could have caused errors in the static sulfur pressure measurements used in this work.

Fluid Bed Sulfur Stripping -

A trial sulfur stripping run was made at an average column temperature of approximately 1050°F in an 8 stage 4"Ø fluid bed regenerator. The results are summarized in Table 38 below.

Table 38. SULFUR STRIPPING IN A CONTINUOUS 8-STAGE FLUID BED

Run No.	Carbon Rate lbs./hr.	Temp. °F (Avg.)	S Loading lb./lb. C		Sulfur Removal %
			In	Out	
SIS-1	31	1048	0.307	.094	66*

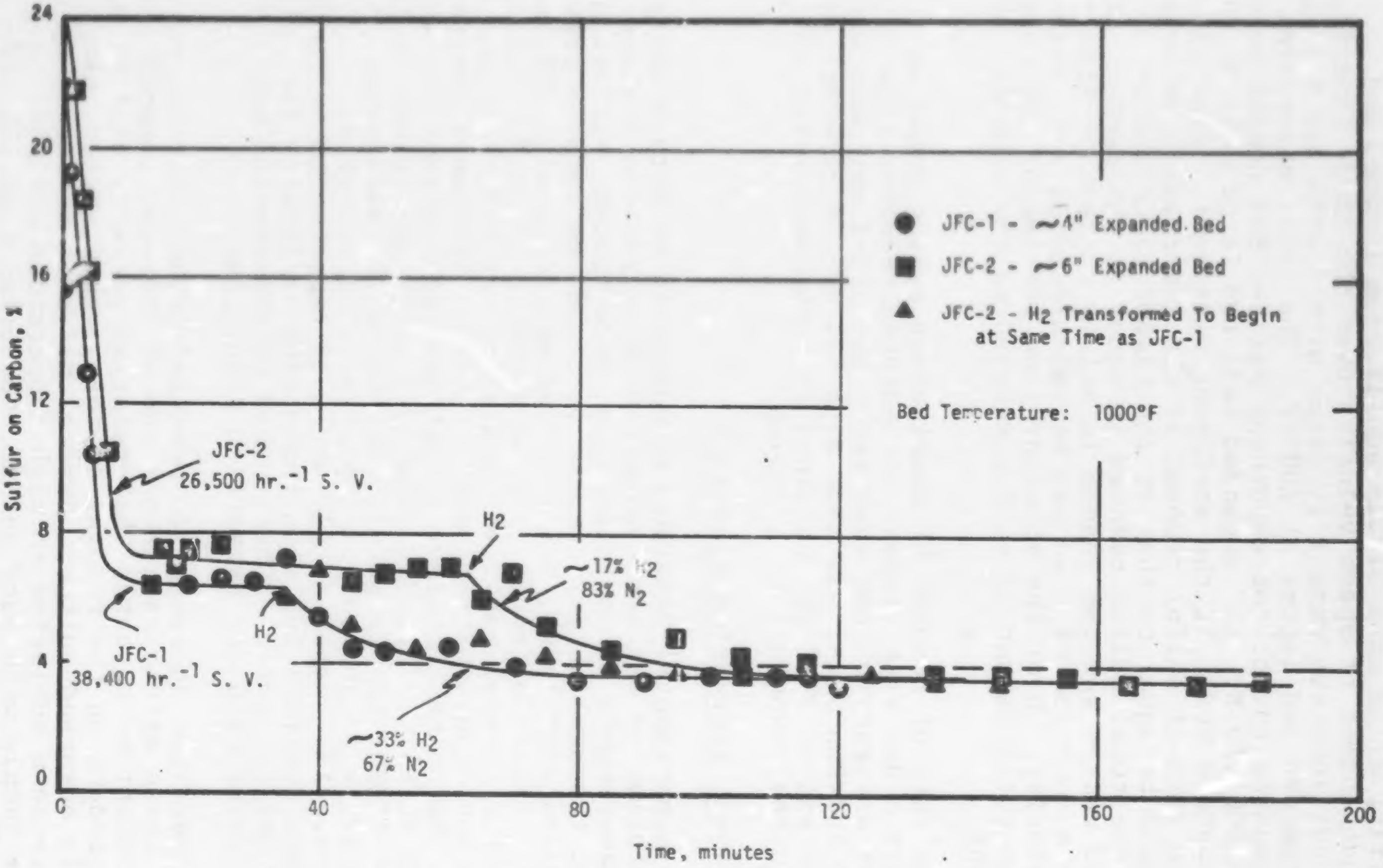
*The removal of 66% of the adsorbed sulfur in the 11 minute residence time compared to 60% obtained previously in a three stage fluid bed unit.

A McCabe-Thiele analysis, assuming 100% stage efficiency, indicated six and a fraction theoretical stages were required to achieve the observed results from the trial run in the 8 stage column. To facilitate the stage efficiency calculation a computer program was written. The program executes an iterative search procedure which converges to an average value of the Murphree tray efficiency over the entire column. For the trial stripping run an efficiency of 79% was calculated. Assuming the data from future sulfur stripping runs yield similar values for the stage efficiency, then the value that is obtained should be a valuable piece of information in designing a sulfur stripper for a particular application.

Bench Scale Sulfur Stripping/H2S Generation -

Two stripping runs were made at 1000°F in the batch 4" electrically heated fluid bed to determine the effect of contact time (space velocity) on the approach to equilibrium in sulfur stripping. Following the stripping of the physically sorbed sulfur, removal of chemisorbed sulfur was investigated as a function of the concentration of the hydrogen reductant. The results of these runs are shown graphically in Figure 55. It appears that the

Figure 55. 4" diameter batch fluidized bed sulfur stripping and hydrogen desulfurization runs (Runs JFC-1 and -2)



stripping is most likely equilibrium limited and independent of space velocity over the range investigated. Conditions run were 2 ft./sec. with 4 inch and 6 inch expanded bed depths at 1000°F. The space velocities corresponding to the corresponding settled bed depths were 38,400 v/v/hr. (4" expanded bed) and 26,500 v/v/hr. (6" expanded bed). If the stripping were equilibrium limited, the rate of sulfur removal at the lower space velocity would be equal to that at the higher space velocity. Since total sulfur removed is equal to the product of the bed weight and the change in sulfur content, sulfur removal as a function of time can be calculated at each space velocity. Over the straight line portion of the curve, the total amount of sulfur removed is the same for the two runs.

The rate of removal of chemisorbed sulfur appeared to be zero order with respect to hydrogen concentration within the accuracy of the analyses. Run JFC-1 was made with 33% H_2 and Run JFC-2 was made with 17% H_2. A constant sulfur content of 3.5% was attained in both cases after 45 minutes' exposure to hydrogen.

Solvent Extraction Studies -

An experimental program was completed to obtain design information for the evaluation of extraction systems. Measurements of sorption rate, pore volume, surface area, and residual sulfur content were made on carbons previously loaded with 14 wt. % sulfur and extracted with $(NH_4)_2C$, CS_2, xylene or ether. The dependence of sulfur loading on sulfur removal was investigated by batch extractions of carbon loaded with 14 wt. % sulfur. This work progressed to the point of carrying out ten-stage extractions with CS_2 at 25°C, 15 wt. % $(NH_4)_2S$ at 40°C, and xylene at 105°C. These experiments were to determine the extraction behavior of the sulfur deposited on the carbon. Physically sorbed sulfur would be expected to be removed quantitatively but with increasing difficulty for sulfur in smaller pores. Chemisorbed sulfur removal would not be expected under extraction conditions.

It was also necessary to measure the SO_2 sorption rates of these extracted carbons and of hydrogen treated carbons. It might be expected that relative activity will be more dependent on the removal of chemisorbed sulfur than physically adsorbed sulfur. Several pairs of extracted samples have been subjected to high temperature (1000°F) purges, one sample with pure helium, the other with 30% hydrogen in the helium. The high temperature purge was an attempt to restore the activity of extracted carbon to the level of virgin carbon. Ether extraction was performed to determine if a sulfur-free extraction solvent, which could be removed from the carbon at low temperatures, would produce an extracted carbon retaining more of its initial SO_2 sorption activity than the other solvents tested. This was primarily aimed at gaining insight into temperature and solvent deactivation effects, not at any potential commercial use of ether as an extraction solvent.

A literature survey on the removal of sulfur by extraction was made. The results of the survey are given in detail in Appendix A-17. Included are sulfur-solvent equilibrium data for ammonium sulfide, carbon disulfide, xylene, benzene, toluene, and pitch oil.

Ammonium Sulfide Extractions -

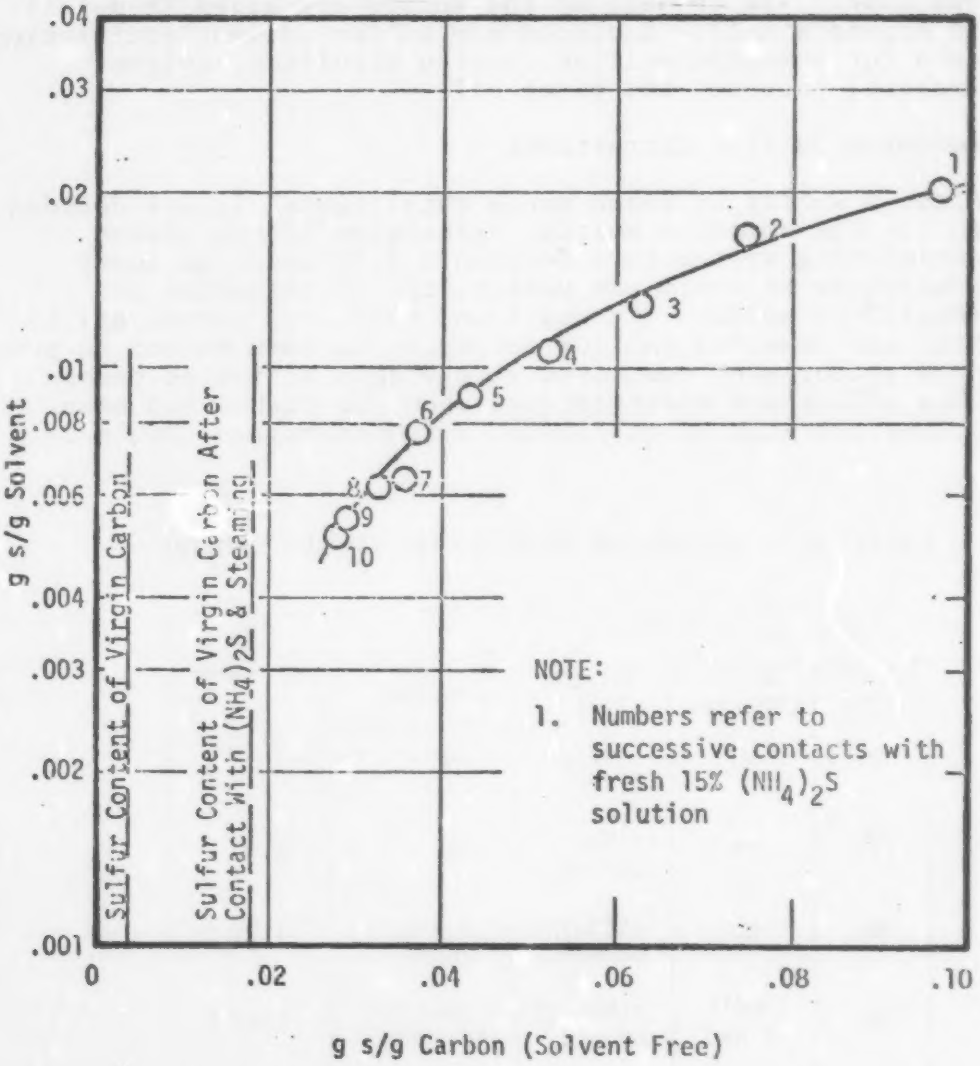
After a series of bench scale extractions, it was decided to run the ammonium sulfide extraction in the closed circulating system (see Section 5.1.7) under an inert atmosphere to avoid any possibility of oxidation of $(NH_4)_2S$ to sulfur. It was found that both carbon disulfide and ammonium sulfide decompose to some extent to produce sulfur when contacted with virgin activated carbon. This effect was observed even when the carbon had been pretreated with N_2 at 1800°F to remove oxygen, Table 39.

Table 39. EFFECT OF SOLVENT ON VIRGIN CARBON

Virgin Carbon C-70-77				0.4% S
Inert Gas	Carbon Degassed	Solvent Wash	Steamed	
NO	No	1xCS_2 30 min.	No	2.2% S
NO	No	1x$(NH_4)_2S$ 30 min.	No	4.0% S
He	No	1x$(NH_4)_2S$ 30 min.	1.5 hrs. 200°F	1.7% S
N_2	1800°F 1 hr.	1x$(NH_4)_2S$ 60 min.	8 hrs. 250-275°F	1.8% S

A ten stage extraction was run in the closed, circulating system. The sulfur level was reduced to 2.08% after the final extraction, washing and steaming. The equilibrium for this system is shown in Figure 56.

Figure 56. Extraction of sulfur loaded activated carbon with 15 weight % $(NH_4)_2S$ solution at 40°C



NOTE:

1. Numbers refer to successive contacts with fresh 15% $(NH_4)_2S$ solution

Carbon Disulfide Extraction -

Carbon disulfide extractions were carried out to determine if carbon disulfide would be superior to ammonium sulfide as an extractant. As shown in Table 39, carbon disulfide contact with virgin carbon was found to have a higher level of residual sulfur (2.2% sulfur) on the carbon than did ammonium sulfide (1.8% sulfur). The decomposition of CS_2 on activated carbon has been enountered previously in the operating experience of textile companies. These companies have, for many years, used large scale activated carbon units for carbon disulfide recovery and air purification. The adsorbed carbon disulfide tends to be hydrolyzed to a small degree, releasing hydrogen sulfide which is oxidized by the air to sulfur. Since this sulfur builds up on the carbon and reduces sorption efficiency, steps are taken to remove it. In the early carbon processes recovering carbon disulfide, this sulfur contaminant was removed by extraction with aqueous sodium sulfide; but present fluid bed recovery plants remove this by continuously stripping a slip stream of the circulating carbon with hot inert gases.

The carbon disulfide extractions were all run on the bench and closely paralleled the results of the ammonium sulfide extraction. The ten stage extraction resulted in a residual sulfur level of 2.6% on the carbon. The equilibrium data for this system are shown in Figure 57.

Xylene Extractions -

A series of bench scale extractions with xylene were carried out in an attempt to obtain lower sulfur levels. The extraction was carried out in five stages, the carbon oven dried and the extraction continued for five additional stages. The sulfur level was found to be nearly independent of sulfur concentration in the solvent. It may be suspected that xylene would be strongly sorbed in the smallest pores and that the residual sulfur would also be concentrated there. A carbon loaded with 14% sulfur was taken to 3.7 g. S/g. carbon after a single contact with xylene at 105°C. Four subsequent contacts for a total of five reduced it to 2.9 g. S/g. carbon. At this point, the carbon was dried in an attempt to bring to the carbon surface a portion of the sulfur contained in the xylene trapped in the smaller pores. This was indicated by both an increase in sulfur concentration in the xylene and a sharp drop in sulfur concentration on the carbon in the sixth extraction. Subsequent extractions followed the pattern of the first five stages. After the tenth stage, the residual sulfur level was reduced to 1.5 g. S/g. carbon. The equilibrium for this system are shown in Figure 58.

Figure 57. Extraction of sulfur loaded activated carbon with CS_2 at 25°C

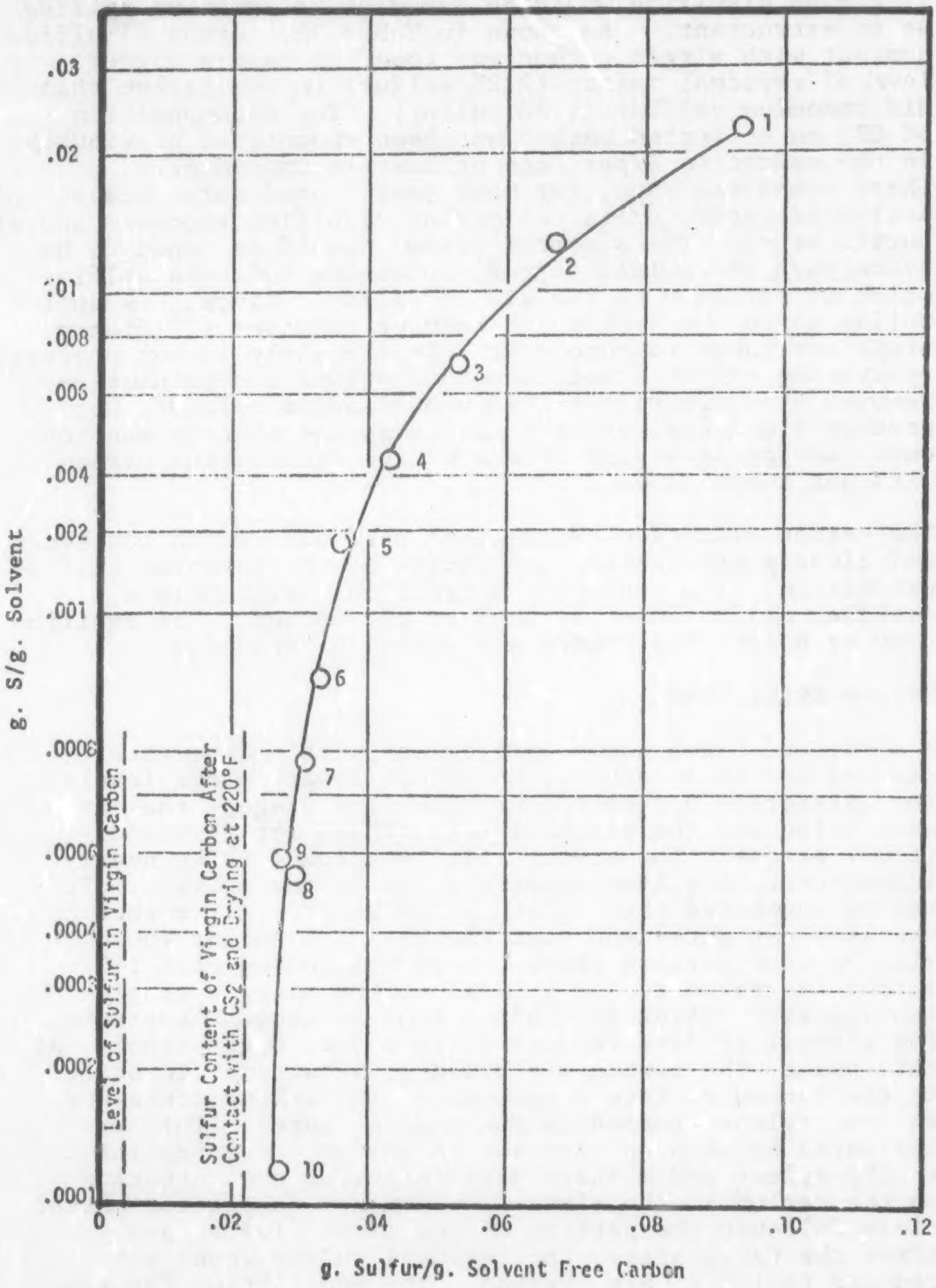
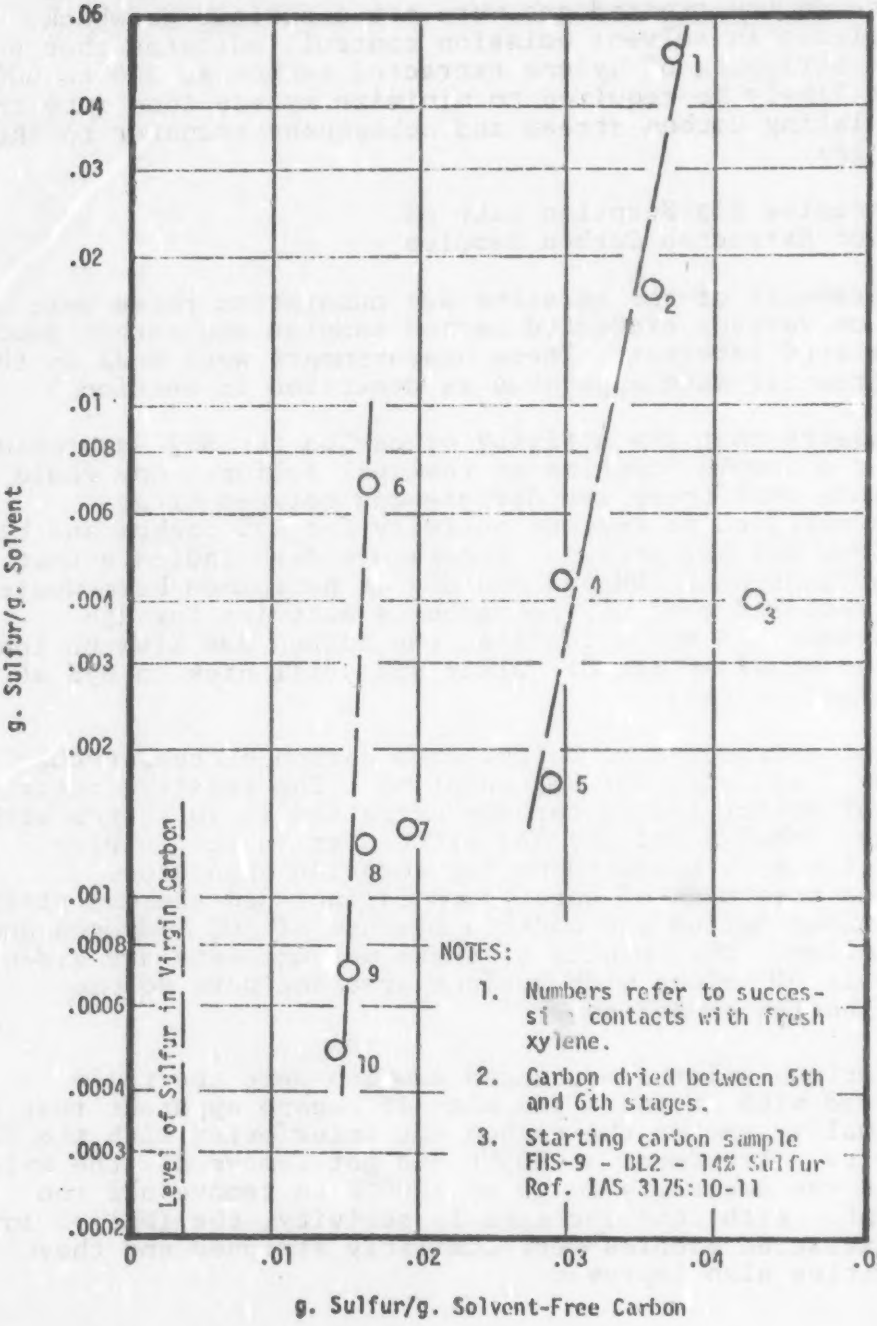


Figure 58. Extraction of sulfur loaded activated carbon with xylene at 105°C



Consideration must be given also to the implications of xylene extraction on the regeneration sequence in a stack gas treating process. Prior applications of xylene extraction have been in applications where trace amounts of xylene in the treated gas were not a serious drawback. Our experience in solvent emission control indicates that a final stripping of xylene extracted carbon at 500 to 600°F would likely be required to minimize xylene loss into the circulating carbon stream and subsequent transfer to the flue gas.

Comparative SO_2 Sorption Rate of Solvent Extracted Carbon Samples -

Measurements of the relative SO_2 adsorption rates were made on various extracted carbon samples and carbon samples of related interest. These measurements were made in the differential rate apparatus as described in Section 5.1.1

It appears that the activity of carbon for SO_2 adsorption is not a simple function of residual sulfur. One would conclude that there are differences between treatments required to restore activity for H_2S pickup and that required for SO_2 pickup. Literature data indicate that extractions with $(NH_4)_2S$ and CS_2 as performed here would have restored most of the carbon's activity for H_2S oxidation. In H_2S oxidation, the carbon may also be loaded with an equal weight of sulfur and still pick up H_2S at a satisfactory rate.

Solvent extraction of sulfur from carbon decreases the carbon's activity for SO_2 sorption. The relative activities of sulfur loaded carbons extracted in 10 stages with xylene, $(NH_4)_2S$ and CS_2 and with ether in the Soxhlet Extractor were measured on the sorption apparatus. Further treatment of these samples included thermal stripping under helium and under a mixture of 30% hydrogen and 70% helium. The results of these measurements are given in Table 40 along with surface area and pore volume distribution comparisons.

The various solvent extracted samples were thermally stripped with an inert gas when it became apparent that the residual xylene on the carbon was interfering with the SO_2 activity. Treatment at 555°F did not remove all the xylene and it was necessary to go to 1000°F to remove all the solvent. With this increase in activity, the $(NH_4)_2S$ and CS_2 extracted samples were similarly stripped and these activities also improved.

Table 40. COMPARISON OF SO_2 ACTIVITY AND SURFACE AREA AND PORE VOLUME MEASUREMENTS

Sample Name	Material	Treatment			% Activity Compared to Virgin Carbon	% Surface Area Compared to Virgin Carbon	% Pore Volume Compared to Virgin Carbon				% Sulfur Residual
		Solvent	Stripping Temp.	Stripping Gas			Total Pores r<500Å Radius	Pores 100<r<500 Å	Pores 10<r<100Å	Pores r<10Å Radius	
EXV-1	Virgin Carbon	None	None	None	100.0	100.0	100.0	100.0	100.0	100.0	0.4
EXN-1	Sulfur Loaded Carbon	None	None	None	—	45.3	47.7	71.6	70.4	39.3	14.0
EXA-1	Sulfur Loaded Carbon	10-Stage Xylene	—	—	7.5	44.8*	47.9	53.2	73.3	39.2	1.47
EXA-2	Sulfur Loaded Carbon	10-Stage Xylene	555°F	Helium	9.4	20.8	24.3	69.4	48.1	15.6	1.20
EXA-3	Sulfur Loaded Carbon	10-Stage Xylene	1000°F	Helium	48.0	80.9	81.0	87.1	81.2	80.8	1.00
EXA-4	Sulfur Loaded Carbon	10-Stage Xylene (2nd Run)	1000°F	Helium	46.0	98.9	99.7	66.1	96.6	101.8	1.76
EXA-5	Sulfur Loaded Carbon	10-Stage Xylene (2nd Run)	1000°F	30% Hydrogen 70% Helium	41.9	93.0	94.0	107.3	96.6	107.8	0.72
EXB-3	Sulfur Loaded Carbon	10-Stage $(NH_4)_2S$	—	—	56.1	96.6	98.1	65.1	100.7	98.4	2.08
EXB-4	Sulfur Loaded Carbon	10-Stage $(NH_4)_2S$	1000°F	Helium	78.6	84.5	83.3	115.3	79.6	83.8	1.28
EXB-5	Sulfur Loaded Carbon	10-Stage $(NH_4)_2S$	1000°F	30% Hydrogen 70% Helium	77.6	90.9	91.1	94.1	84.8	93.0	1.36
EXC-1	Sulfur Loaded Carbon	10-Stage CS_2	—	—	45.4	101.9	102.2	65.1	107.3	101.8	13.20
EXC-2	Sulfur Loaded Carbon	10-Stage CS_2	1000°F	Helium	63.0	91.6	91.2	92.9	89.4	91.7	1.20
EXC-3	Sulfur Loaded Carbon	10-Stage CS_2	1000°F	30% Hydrogen 70% Helium	57.2	93.6	92.8	85.9	82.6	96.3	1.36
EXE-1	Sulfur Loaded Carbon	Ether (Soxhlet)	—	—	46.1	19.7	23.3	70.6	53.2	12.5	2.60

*Underlined numbers are corrected values.

From earlier work on hydrogen treatment of regenerated samples, we found a return of activity for SO_2 when the sample was stripped at 1000°F with 33% H_2 in helium. In addition, a similar sample treated at 1500°F increased its activity 65% over the virgin material. In view of these earlier results, we decided to run parallel extracted samples in which 30 volume % H_2 was added to the helium purge gas at 1000°F. The activities remained essentially unchanged with H_2 added to the purge gas. However, the pore volume, surface area and residual sulfur measurements indicate that the bench scale stripping conditions chosen were not sufficient to give good sulfur removal from the smallest pores. The hydrogen flow was much lower than used in earlier work on hydrogen regeneration. Replicate runs will be made at higher purge rates to allow further evaluation of the solvent extracted carbon's ability to be restored to its original activity by hydrogen treatment.

Conclusions which may be drawn from the data at this point are as follows. Xylene appears to be an inferior extraction solvent for sulfur, due to the difficulty in removing it from carbon and some residual solvent deactivation effect which persists, even through a high temperature hydrogen treatment. Ammonium sulfide and carbon disulfide appear to be close in effectiveness. However, the ammonium sulfide appears to have a lesser residual solvent deactivation effect when the carbon is given either a high temperature treatment with inert gas or hydrogen.

Indications are that ether has no less of a solvent deactivation effect on carbon than does carbon disulfide, and the solvent deactivation effect is not strongly influenced by the presence of sulfur in the solvent structure.

While it appears that a return of surface area or pore volume will not guarantee a return of activity for SO_2, a significant loss of either will indicate a loss in activity for SO_2. Similarly, high residual sulfur content will tend to cause activity loss, but poor activity can persist even at low residual sulfur levels.

The indication that iso-thermal regeneration is as effective as high temperature regeneration is somewhat clouded by the mild regeneration conditions. As one attempts to return carbon to its original activity, chemisorbed oxygen prevents this unless higher temperatures are used. Hydrogen is believed to remove the chemisorbed oxygen at lower temperatures. Chemisorbed oxygen also has a cumulative effect under recycle conditions.

Recycle Work - Extraction Regeneration vs. Thermal/Reduction Regeneration -

Two samples of carbon were recycled through the adsorption and regeneration steps to allow a direct comparison of the isothermal (extraction) and thermal regeneration sequences. The experiments also showed the effect of recycle on the SO_2 activity of the carbon for each of the two regeneration sequences. The results of the study were: 1) that the SO_2 activity of thermal/reductive regenerated carbon leveled off at about 92% of the activity of the virgin carbon, and 2) that the SO_2 activity of the isothermally [$(NH_4)_2S$] regenerated carbon decreased gradually with each cycle and after 6 cycles was at about 34% of the activity of the virgin carbon. Pore volume measurements showed a decrease in the total pore volume and surface area of the isothermally regenerated sample and an increase in total pore volume and surface area of the thermally regenerated sample. The SO_2 sorption differential rate apparatus was shown to be useful in assessing various treatments of the $(NH_4)_2S$ extracted sample after six cycles.

Details of the recycle experiments are given in Appendix A-15.

Experimental Results and Discussion -

A recycle series was run to compare the isothermal (extraction) and thermal/reductive regeneration sequences. Sample A will be referred to as the isothermally regenerated carbon and Sample B referred to as the thermally regenerated carbon. Samples A and B were loaded with acid, reacted with H_2S to form sulfur on the carbon, and then regenerated by $(NH_4)_2S$ extraction or thermally with H_2, respectively. The sequence in the cycling was as follows:

A. Isothermal	B. Thermal/Reductive
1. SO_2 sorption	1. SO_2 sorption
2. Sulfur generation	2. Sulfur generation
3. Sulfur extraction with $(NH_4)_2S$ followed by steaming	3. High temperature H_2-S reaction on carbon

Each sample was then passed through successive complete cycles. The SO_2 sorption step on each cycle provided a means of comparing SO_2 activities to the virgin material. As a basis for comparing SO_2 activity, the acid loading at 210 minutes relative to the virgin material was defined as the SO_2 activity.

$$SO_2 \text{ Activity} = \frac{\text{Acid Load. at 210 Min. for Sample A or B for Cycle } i}{\text{Acid Load. at 210 Min. for Virgin Carbon}} \qquad (47)$$

The rate of SO_2 sorption is a function of temperature. Variation in the average sorption temperature for any cycle was corrected back to average temperature for loading the virgin material with acid. The Westvaco equation was used as a guide to make this correction, T_F:

$$T_F\text{, Temperature Correction Factor, } = \frac{5520\,(T_{virgin} - T_{cycle\ i})}{T_{virgin}\,T_{cycle\ i}} \qquad (48)$$

where T_{virgin} = sorption temperature at which virgin material is loaded, °R
$T_{cycle\ i}$ = sorption temperature at which sample is being loaded in cycle i

The sulfur remaining on the carbon after isothermal or thermal treatment varied between 2 and 4% S. In order to compare SO_2 activities at comparable sulfur loadings, the SO_2 activity was corrected to a common sulfur level of 2%. Previous work, in which varying amounts of sulfur were sorbed on activated carbon, was used to make this sulfur correction. The results of the work are shown in Figure 59. The sulfur correction factor, S_F, is given as

$$S_F\text{, S Correction Factor to 2\% S Basis, } = \frac{\text{Activity at \% } S_i}{\text{Activity at 2\% S}} \qquad (49)$$

$$= \frac{\text{Activity at \% } S_i}{0.909}$$

The recycle work with the respective correction factors is summarized in Table 41. The final SO_2 activity is calculated by multiplying the uncorrected SO_2 activity by

Figure 59. Effect of percent sulfur on carbon on the SO_2 activity

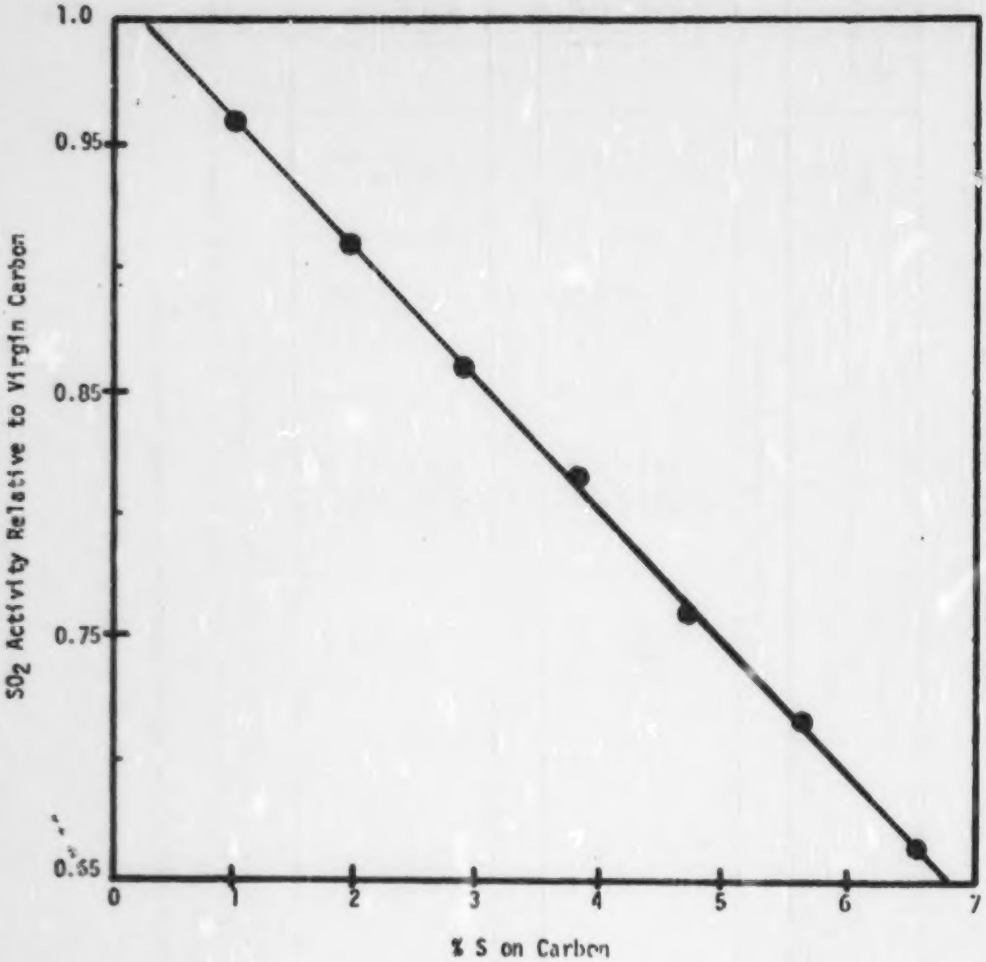


Table 41. EFFECT OF RECYCLE ON SO_2 ACTIVITY FOR ISOTHERMAL AND THERMAL/REDUCTIVE REGENERATIONS

Run Number	Sulfuric Acid Loading at 210 Minutes, gms H_2SO_4/gm Carbon	Uncorrected SO_2 Activity	Average SO_2 Sorption Temperature		Per Cent Sulfur, %	Sulfur Correction Factor to 2% S Basis	SO_2 Activity
			°F	Correction Factor			
Thermal/Reductive Regenerations							
RXT-6-1A*	0.155	1	207.4	1	0.4	0.909	0.909
-2A	0.140	0.903	209.3	1.0233	2.6	1.041	0.962
-3A**	0.145	0.935	198.8	0.8950	3.3	1.032	0.905
-4A	0.144	0.929	203.2	0.9489	2.6	1.038	0.915
-5A	0.136	0.877	205.5	0.9766	3.2	1.077	0.922
-6A	0.140	0.903	198.2	0.8815	3.6	1.181	0.940
Ammonium Sulfide Extraction Regenerations							
RXT-7-1A***	0.167	1	205.0	1	0.4	0.909	0.909
-2A	0.077	0.461	202.4	0.9679	4.1	1.143	0.510
-3A	0.090	0.539	203.7	0.9838	3.1	1.072	0.568
-4A	0.072	0.431	205.5	1.0063	2.1	1.053	0.457
-5A	0.054	0.323	204.5	0.9938	2.9	1.057	0.339
-6A	0.062	0.371	203.2	0.9776	2.0	1	0.363

*Virgin carbon is -1A;and -6- signifies thermal regeneration.

**Humidifier temperature was low, correction factor for lower moisture content using Westvaco Equation = 1.0712.

***Virgin carbon is -1A; and -7- signifies isothermal regeneration.

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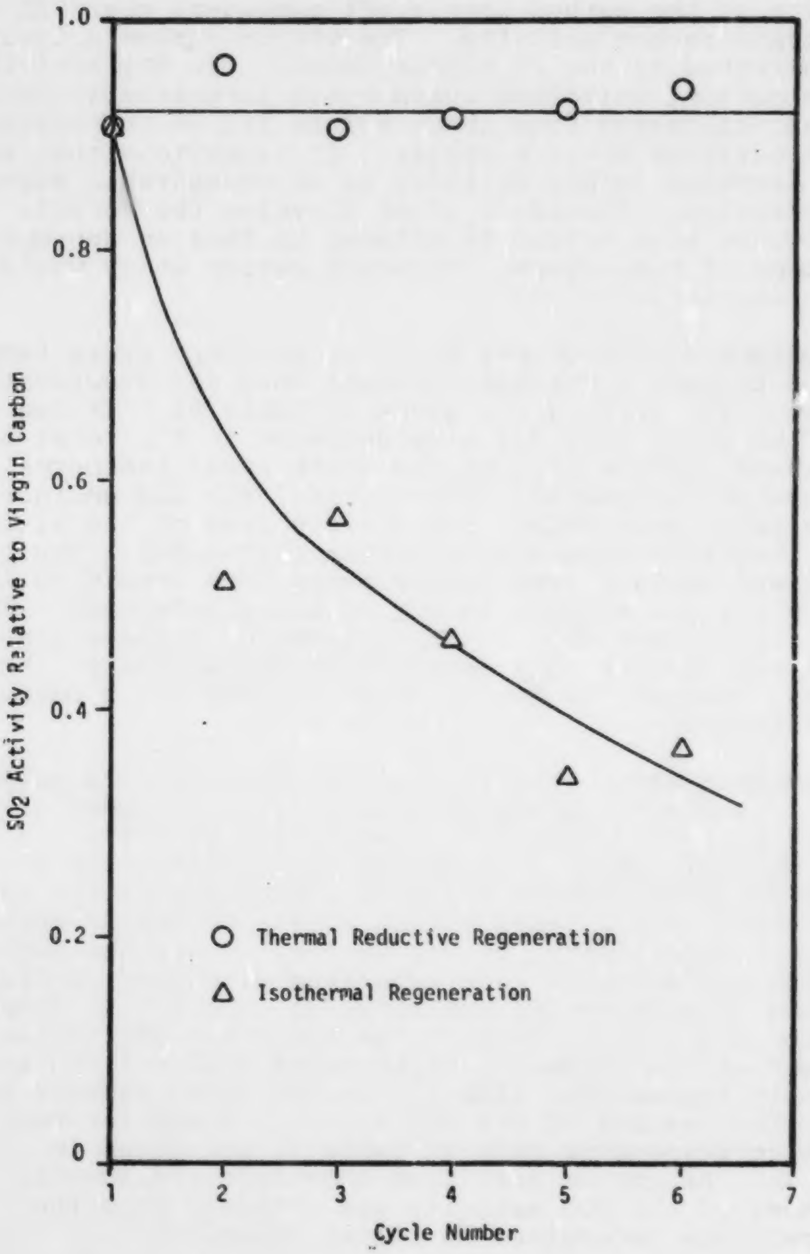
the two correction factors for temperature and sulfur level. The SO_2 activity is shown as a function of the cycle number in Figure 60. As can be seen from Figure 60 and Table 41, for the thermal/reductive sequence the SO_2 activity of the carbon levels off somewhere near 92% of the virgin carbon activity. The virgin carbon activity was corrected to the 2% sulfur level. The SO_2 activity of the carbon, which was regenerated isothermally using $(NH_4)_2S$, decreased from about 60% to 34% of the original carbon activity after 6 cycles. It is obvious that this rapid decrease in SO_2 activity is an undesirable aspect of extraction. Therefore after 6 cycles the recycle experiments were halted to attempt to find an appropriate treatment of the solvent extracted carbon which would return its activity.

Pore volume distributions were run on sixth cycle Samples A and B to gain a possible insight into the deactivation process. The results are given in Table 42. It can be seen that there is a definite decrease in the total pore volume and surface area of the sixth cycle isothermally regenerated (extracted) carbon (RXT-7-6C) and an increase in the total pore volume and surface area of the sixth cycle thermally regenerated carbon (RXT-6-6C). The pore volume and surface area measurements have seemed to indicate only gross effects in SO_2 activity reduction. That is, a significant drop in pore volume or surface area definitely results in a decrease in SO_2 activity. Small changes, however, do not necessarily indicate a decrease in SO_2 activity.

As mentioned above, the recycle experiments were stopped after 6 cycles to assess an appropriate treatment of the $(NH_4)_2S$ extracted carbon to restore its activity. Since there was only about 30 grams of this sixth cycle carbon, it was desirable to use as small a quantity of the sample as possible, but a large enough sample to assess each treatment experiment. It was decided to use the SO_2 sorption differential rate apparatus discussed in previous sections to measure SO_2 activity, as only 0.1 g. samples are required. As a check on the fixed bed SO_2 sorber, two each of the thermally regenerated (RXT-6-) and isothermally regenerated (RXT-7-) carbon cycle samples were used. The results of the SO_2 activity found for each of the corresponding runs in Table 41 are given in Table 43. As can be ssen from the table, reasonably good agreement of the SO_2 activity was obtained from the integral rate determined in either apparatus.

Figure 60. Effect of recycle on SO_2 ability for isothermal and thermal/reductive regenerations*



*All points have been corrected to a 2% sulfur basis.

Table 42. PORE VOLUME DISTRIBUTION RESULTS USING ENGELHARD ISORPTA APPARATUS

Sample	% Pore Vol. Compared to Virgin Carbon				% Surface Area Compared to Virgin Carbon
	Total Pores <500A	Pores 100-500A	Pores 10-100A	Pores <10A	
EXV-1 (Virgin Carbon)	100	100	100	100	100
RXT-6-6C (Thermal)	118	77.1	114	121.0	119.0
RXT-7-6C (Extracted)	93.8	67.0	95.4	94.2	92.6

Table 43. SO_2 ACTIVITIES INTEGRAL RATE DETERMINED USING DIFFERENTIAL RATE APPARATUS VERSUS USING FIXED BED

Run	SO_2 Activity for Differential Bed*	SO_2 Activity**	
		Differential Bed	Fixed Bed
RXT-6-4A	0.834	0.866	0.915
RXT-6-6A	0.818	0.966	0.940
RXT-7-4A	0.426	0.449	0.457
RXT-7-6A	0.397	0.397	0.363

*Uncorrected to 2% S basis.
**Corrected to 2% S basis.

Treatments To Restore SO_2 Activity of Solvent Extracted Carbon

The sixth cycle carbon sample from the isothermal regeneration recycle studies which had about 34% of its original activity was put through a number of post treatments, which were assessed as to their success in restoring the SO_2 sorption activity. The SO_2 sorption differential rate apparatus was used to make the evaluation of the success of each of the post treatments. The experiments included both isothermal and thermal treatments. The runs, respective post treatments, and activity measurements are summarized in Table 44.

From the data given in Table 44 it can be seen that the post treatment experiments included the determination of:

1) Isothermal NH_4OH treatment to remove the sulfate or other possible deactivation species
2) Effect of treatment time with H_2
3) Effect of treatment temperature
4) Effect of using heat only
5) Effect of using CO as the reductant.

The isothermal treatment with NH_4OH was unsuccessful in returning the SO_2 activity of the solvent extracted carbon. In fact, some further deactivation was noted. For comparison purposes virgin carbon showed a drop in activity to 60% of its original value upon being treated with the NH_4OH experimental step.

The effect of treatment time using H_2 at 1000°F is also shown in Figure 61. The increase in the SO_2 activity is less rapid with increasing treatment time. It appears that the optimum time in a fixed bed would be 4 to 6 hours.

The effect of temperature using H_2 for a 4 hour treatment is also shown in Figure 62. The SO_2 activity of the $(NH_4)_2S$ extracted sample increases rapidly with treatment temperatures from 800 to 1200°F. SO_2 activities of more than 130% of the original value can be obtained at 1200°F with a 4 hour treatment time. It appears that the lower limit of temperature for H_2 treatment might be near 800°F.

It is seen from the experiment using N_2 at 1000°F that although heating is giving some increase in SO_2 activity, the H_2 is playing a definite added role of reactivation. The N_2 treated sample at 1000°F had an SO_2 activity of

Table 44. EFFECT OF POST TREATMENTS OF (NH4)2S EXTRACTED SIXTH CYCLE CARBON ON SO_2 ACTIVITY

Run Number	Sample	Treatment			H_2SO_4 Loading** mgs. Acid/gm. C	Uncorrected SO_2 Activity	Sulfur %	Sulfur Correction Factor*	SO_2 Activity Corrected to 0.8% S Basis
		Gas	Temp., °F	Time, hrs.					
160-G	Virgin				173.90	1.000	0.4	0.988	0.988
197-G	RXT-7-6C				63.17	0.363	2.1	1.076	0.391
191-G	RXT-7-6C-4	30% H_2	800	4	116.69	0.671	0.8	1.000	0,671
189-G	RXT-7-6C-1	30% H_2	1000	2	160.87	0.925	0.9	1.005	0.929
193-G	RXT-7-6C-6	30% H_2	1000	4	184.95	1.064	0.8	1.000	1.064
192-G	RXT-7-6C-5	30% H_2	1200	4	234.49	1.348	0.8	1.000	1.348
194-G	RXT-7-6C-7	N_2	1000	4	88.37	0.508	0.6	0.988	0.502
195-G	RXT-7-6C-8	30% CO	1000	4	131.29	0.755	1.0	1.005	0.759
196-G	RXT-7-6C-9	2% NH_4OH; Purged 1 hr. with N_2 at 400°F			58.56	0.337	1.4	1.034	0.348
198-G	Virgin	2% NH_4OH; Purged 1 hr. with N_2 at 400°F			119.32	0.686	0.7	0.995	0.655

*Using relationship developed of effect of sulfur on SO_2 activity.

**To 210 minutes sorption time.

Figure 61. Effect of treatment time using hydrogen post treatment of $(NH_4)_2S$ extracted sample of sixth cycle

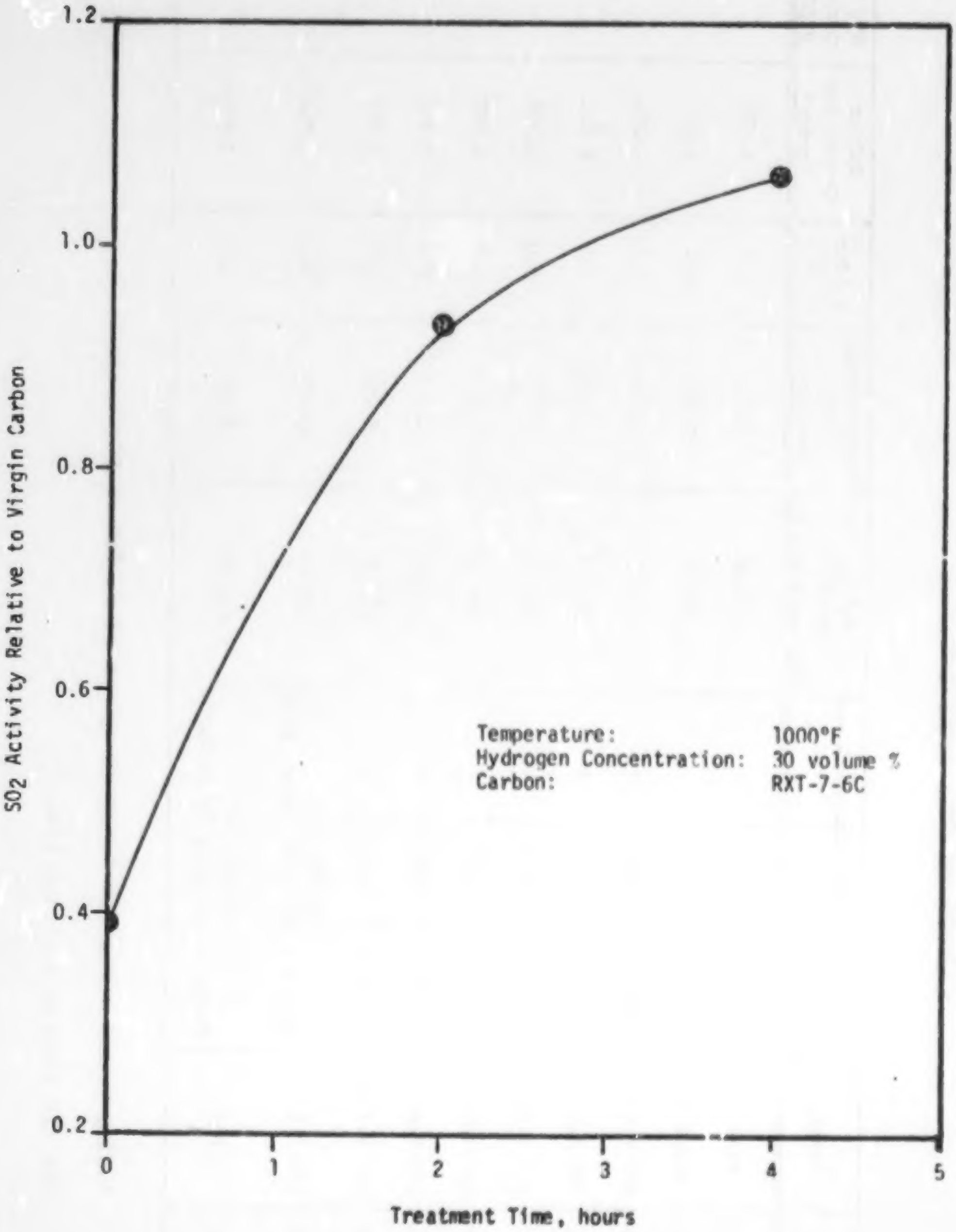
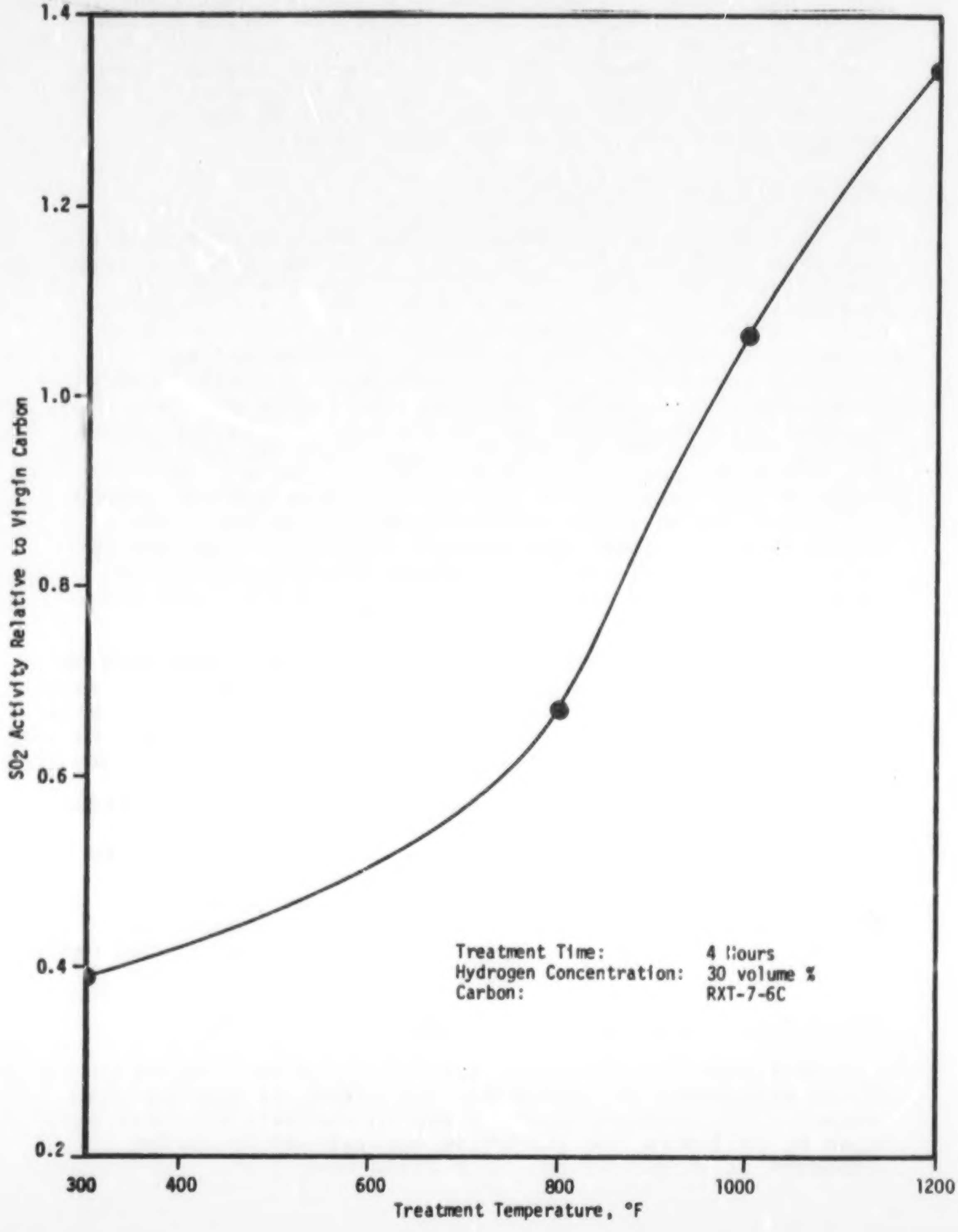


Figure 62. Effect of temperature of hydrogen post treatment of (NH4)2S extracted sample of sixth cycle



about 50%, whereas the H_2 treated sample at 1000°F had about 90% of its original activity of the virgin carbon. The CO treated sample had an activity of about 75% which lies somewhere between the two extremes of thermal treatment only and thermal/reductive H_2. This gives even more support to the definite beneficial effect H_2 has on returning the activity of activated carbon.

5.2.4 H_2S Generation

Hydrogen is the basic reductant that is used to reduce the sulfuric acid sorbed on the carbon. It was found, however, that a secondary reductant produced from the hydrogen, hydrogen sulfide, is a better reductant of the sulfuric acid. Sulfuric acid reduction was found to occur in the temperature range of 200 to 300°F, as discussed in a previous section, so process development proceeded toward producing this recycled reductant within the process. The initial process concept was to vaporize the sulfur, originating from the SO_2 in the flue gas, from the carbon. The remaining recycled sulfur on the carbon was then reacted with hydrogen to form the hydrogen sulfide needed to reduce the sulfuric acid to elemental sulfur. The major deviation from that initial concept is that the two unit operations of sulfur stripping and H_2S generation have been combined successfully into a single fluid bed reactor as discussed in a later section.

In this section, the bench scale data that was developed on the kinetics of H_2S formation from hydrogen and sulfur vapor over a catalyst of activated carbon is discussed. The pilot work that was done on this unit operation is discussed in the later section on combined sulfur stripping/H_2S generation.

In addition to the use of hydrogen for sulfuric acid reduction by way of hydrogen sulfide, other possibilities of hydrogen requirements are hydrogen to remove chemisorbed oxygen from the reused activated carbon and, hydrogen chemisorption by the regenerated activated carbon.
The chemisorbed O_2 is discussed under the integral run results. The studies of H_2 chemisorption on activated carbon are discussed in this section.

Fixed Bed Studies H_2 Chemisorption -

The objectives of the study were to ascertain the extent of H_2 chemisorption on carbon and the effect of cycling the carbon. The general approach was to evaluate H_2 chemisorption by following the gas phase analysis of H_2 during exposure of virgin carbon in a fixed bed.

The next step, not initiated, was to start a recycle bench scale experiment in which virgin carbon is loaded with SO_2, reacted to form S, then exposed to H_2 to convert the sulfur to H_2S and to measure the H_2 chemisorbed. During the runs the off-gas from each process step would be analyzed by gas chromatograph. The carbon at the end of each cycle would be analyzed for total sulfur content and for SO_2 activity in a differential SO_2 sorber as a check on the SO_2 sorption step. It was anticipated initially to complete six cycles. This second part of the study was not completed because of the delay that would follow in completing the integral run.

The major response was the amount of H_2 chemisorbed either on virgin carbon or on recycled carbon. Secondary responses were the SO_2 activity of recycled carbon and the effect of recycle on conversion of sorbed H_2SO_4 to S and of the sulfur to H_2S, and on H_2 chemisorption.

H_2 Chemisorption on Virgin Carbon -

The virgin carbon was heated to about 1850°F in an inert atmosphere to purge off any chemisorbed oxygen. The sample was then cooled to the indicated temperature under an inert purge and H_2 introduced to the reactor at the indicated concentration. During all phases of treatment the off-gas was analyzed using a gas chromatograph.

Recycle Experiments - H_2 Chemisorption on Recycled Carbon -

Virgin carbon was to be loaded with H_2SO_4, reacted with H_2S to form elemental sulfur, and then treated at 1200°F with 30 vol. % H_2 to form H_2S and measure chemisorbed H_2. During each process step the off-gas was to be analyzed with the gas chromatograph or SO_2 analyzer. The carbon was then to be analyzed for SO_2 activity and recycled through each process step again.

Run Conditions -

The run conditions initially anticipated are listed in Table 45.

The first H_2 chemisorption studies on the bench scale were planned using virgin carbon, but the original equipment and procedures used were unsatisfactory for detecting H_2 chemisorption. Five experiments indicated that either no H_2 was chemisorbed or that the process was so fast that the chemisorption could not be detected with the restraint that a gas analysis could only be made every 12 minutes.

Table 45. PLANNED EXPERIMENTAL PROGRAM FOR STUDYING HYDROGEN CHEMISORPTION ON ACTIVATED CARBON DURING REGENERATION OF THE CARBON

<table>
<tr><th>Run</th><th colspan="2">Inlet H_2 Conc. Vol. %</th><th colspan="3">Grams Carbon</th><th>Lin. Gas Velocity ft./sec.</th><th>Space Velocity $hr.^{-1}$</th><th>Temp. °F</th><th>Effect</th><th>Purpose</th></tr>
<tr><td>HCS-1</td><td colspan="2">38</td><td colspan="3">15.2</td><td>0.20</td><td>1300</td><td>1200</td><td>Temperature</td><td rowspan="5">H_2 Chemisorption on Virgin Carbon</td></tr>
<tr><td>HCS-2</td><td colspan="2">38</td><td colspan="3">16.2</td><td>0.20</td><td>1300</td><td>1000</td><td>"</td></tr>
<tr><td>HCS-3</td><td colspan="2">38</td><td colspan="3">17.3</td><td>0.20</td><td>1300</td><td>800</td><td>"</td></tr>
<tr><td>HCS-4</td><td colspan="2">20</td><td colspan="3">15.2</td><td>0.20</td><td>1300</td><td>1200</td><td>Inlet H_2 Conc.</td></tr>
<tr><td>HCS-5</td><td colspan="2">10</td><td colspan="3">15.2</td><td>0.20</td><td>1300</td><td>1200</td><td>"</td></tr>
<tr><th rowspan="3">Run</th><th colspan="5">Inlet Gas Conc.</th><th rowspan="3">Grams Carbon</th><th rowspan="3">Lin. Gas Velocity ft./sec.</th><th rowspan="3">Space Velocity $hr.^{-1}$</th><th rowspan="3">Temp. °F</th><th rowspan="3">Purpose</th></tr>
<tr><th rowspan="2">SO_2 PPM</th><th rowspan="2">NO PPM</th><th colspan="3">Vol. %</th></tr>
<tr><th>N_2</th><th>O_2</th><th>H_2O</th></tr>
<tr><td>* HCS-6-A-_</td><td>2500</td><td>150</td><td>Bal.</td><td>3.5</td><td>10</td><td>15</td><td>0.18</td><td>3,000</td><td>200</td><td rowspan="5">Effect of Recycle on H_2 Chemisorption</td></tr>
<tr><th>Run</th><th colspan="2">Inlet H_2S Conc. Vol. %</th><th colspan="3">Grams Carbon</th><th>Lin. Gas Velocity ft./sec.</th><th>Space Velocity $hr.^{-1}$</th><th colspan="2">Temp. °F</th></tr>
<tr><td>HCS-6-B-_</td><td colspan="2">30</td><td colspan="3">14</td><td>0.014</td><td>200</td><td colspan="2">300</td></tr>
<tr><th>Run</th><th colspan="2">Inlet H_2 Conc. Vol. %</th><th colspan="3">Grams Carbon</th><th>Lin. Gas Velocity ft./sec.</th><th>Space Velocity $hr.^{-1}$</th><th colspan="2">Temp. °F</th></tr>
<tr><td>HCS-6-C-_</td><td colspan="2">30</td><td colspan="3">15</td><td>0.20</td><td>1300</td><td colspan="2">1200</td></tr>
</table>

*Run HCS-6-_-_

→ Denotes cycle number

→ A denotes SO_2 sorption.
→ B denotes sulfur generation.
→ C denotes H_2S generation.

Therefore a different equipment setup was used which was composed of a thermal conductivity cell as used on a gas chromatograph. A schematic of the equipment used is shown in Figure 63. A major difference in this setup is that the off-gas from contact with the carbon is analyzed continuously. The experimental procedure was as follows:

1) The virgin carbon was heat treated at 1800°F with 120 scc/min. of N_2 (R-1) for 3 hours.

2) The sample was cooled to room temperature at the same N_2 flow rate.

3) The detector was calibrated. The H_2/N_2 mixture (about 30%) was passed through the reference side of the detector and known mixtures were passed through the other side of the detector. The resultant responses were plotted and served as a calibration curve.

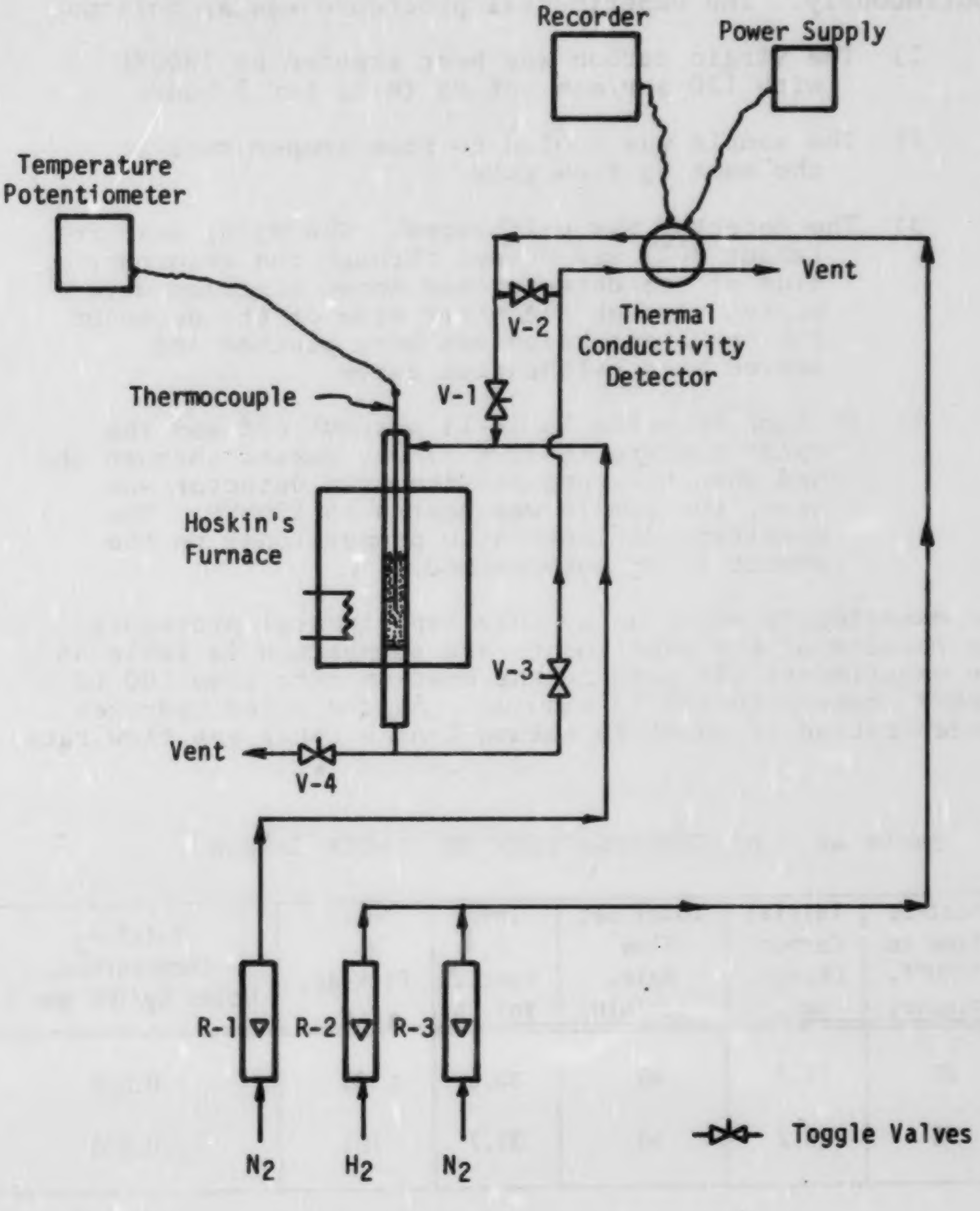
4) At time zero, the N_2 (R-1) was cut off and the H_2/N_2 mixture (R-2, R-3) was passed through the bed when the response from the detector was zero, the sample was heated to 1200°F. The resultant deflection is proportional to the amount of H_2 chemisorbed.

Two experiments were run by this experimental procedure. The results of the experiments are summarized in Table 46. The experiments differed in the heat-up rate from 100 to 1200°F, namely 20 and 75 minutes. At the inlet hydrogen concentration of about 30 volume % at a total gas flow rate

Table 46. H_2 CHEMISORPTION ON VIRGIN CARBON

Run	Heat-up Time to 1200°F, minutes	Initial Carbon Charge, gms.	Total Gas Flow Rate, scc/min.	Inlet H_2 Conc., Vol. %	Total H_2 Pick-up, scc	Total H_2 Chemisorbed, moles H_2/100 gms C
HCS-8	20	15.2	49	30.6	85	0.026
HCS-9	75	15.2	50	31.7	101	0.030

Figure 63. Equipment schematic for H_2 chemisorption experiments on virgin carbon


Recorder
Power Supply
Temperature Potentiometer
Vent
V-2
Thermal Conductivity Detector
Thermocouple
V-1
Hoskin's Furnace
V-3
Vent
V-4
R-1
R-2
R-3
N2
H2
N2
Toggle Valves

of 50 scc/min. the amount of H_2 chemisorbed was about 0.028 moles H_2/100 gms carbon. In earlier experiments, the amount of H_2 unaccounted for was of the order of 0.1 moles H_2/100 gms carbon. Therefore only about 30% of the necessary H_2 is accounted for if the H_2 chemisorption phenomena is similar on virgin carbon and sulfur loaded carbon.

There are a number of factors which make determination of H_2 chemisorption on sulfur loaded carbon difficult to determine on the bench scale. These include the following:

1) The bench scale is at unsteady state.

2) The phenomena of H_2 chemisorption is apparently fast at the temperatures of H_2S generation.

3) The system for continuous analysis (Figure 63) is only suitable for a two component system (inert of N_2 + one other component such as H_2), but during H_2S generation, H_2S is also formed, as well as a number of other possible compounds.

4) All of the problems mentioned above would probably lead to difficulties in setting up an analytical system with available equipment for studying H_2 chemisorption as a function of cycling on the bench scale.

5) Because of the difficulties mentioned in Step 4 a delay in achieving integral operation was anticipated.

Further analysis of the impact of the possible increased H_2 requirements due to H_2 chemisorption was made as to the effect on overall process economics. The process economics were assessed on the basis of 20% additional H_2 required. The results based on a previous economic analysis by Westvaco, which should at least indicate the relative cost increases even if the economic bases may have changed somewhat. There is a projected increase in costs of about 1.7% in the capital costs and about 3% in the operating costs for a 1,000 MW installation.

At this time a program that lead to integration and operation of the pilot plant for repetitive cycling of the carbon was being pursued. It was felt and shown that this operation gave a good indication of the hydrogen requirements on a long term basis. Preliminary bench scale tests indicated that complete definition of the hydrogen use in an unsteady state system would require significant effort and instrumentation not available at this time.

Any further effort on bench scale experiments would have delayed the integration of the pilot plant and it was felt that further consideration of bench scale work was not justified. This was based on the minimal impact of the increased hydrogen use on economics and anticipated data that was obtained in the pilot plant.

H_2S Generation Kinetic Studies -

The first runs were made to find the effects of H_2 concentration, and sulfur vapor concentration on the formation of H_2S with and without activated carbon as a catalyst. Conditions for these runs are listed in Table 47.

Table 47. EXPERIMENTAL CONDITIONS FOR H_2S GENERATION RATE EXPERIMENTS

	Run I	Run II
Inlet H_2 Conc.	28.5%	18.9%
Inlet S Conc. as S_1	6.36%	7.13%
Total Flow Rate	645 cc/min. STP	625 cc/min. STP
Reaction Temperature	1000°F	1000°F
Linear Veloc. @ 1000°F	0.22 ft./sec.	0.21 ft./sec.
Bed Depth	0.2 inch	0.2 inch
Space Veloc. @ 1000°F	47,800 $hr.^{-1}$	46,200 $hr.^{-1}$
Carbon Weight	1.65 gm	
Carbon Type	Virgin WV-W 12x40, Log C-70-30	
Empty Reactor Volume	0.00273 $ft.^3$	
Carbon Bed Volume	0.0000908 $ft.^3$	

Homogeneous Reaction -

The reactor system was constructed with two identical reactor tubes, one of which contains a carbon sample and another which is empty. Reference to the homogeneous reaction indicates reaction in the empty tube although, of course, there may be some influence of the tube wall. Rate determinations were made by measuring the steady state concentrations of H_2S in the effluent gas and calculating rate of formation using the total gas flow rate. Based on the reactor volume inside the reactor furnace held at 1000°F, the rates of formation were found to be 0.054 lb. mol/hr./ft.^{3} and 0.038 lb. mol/hr./ft.^{3} for Runs I and II, respectively, under the conditions listed in Table 47.

These results may be compared to the rates derived from kinetic data of Aynsley, Pearson and Robinson[4] and of Norrish and Rideal[5]. In each case these authors' data yielded good straight line plots according to the expression

$$\frac{dR_{H_2S}}{dt} = k[S]^{1/2}[H_2S] \qquad (50)$$

where $k = Ae^{-E/RT}$

when the calculated values of ln k from their data were plotted against 1/T over their experimental range of 550-650°F. Using values of k so extrapolated to 1000°F, reaction rates were calculated for the present experimental conditions and are compared in Table 48.

Table 48. COMPARISON OF H_2S FORMATION RATES FROM LITERATURE AND EXPERIMENTAL DATA (HOMOGENEOUS)

Source	Rate at Inlet Conditions at at 1000°F (lb. mol/hr./ft.^{3})		k
	Run I	Run II	
Anysley	0.00024	0.00017	23
Norrish	50.6	35.5	4,800,000
Experimental	0.054	0.038	5,024 (I) 5,270 (II)

As seen, the present experimental data fell between the widely separated literature data although somewhat closer to that of Aynsley. No adjustment of the present experimental data for the difference between inlet and outlet concentrations or the residence time in zones below 1000°F in the reactor can account for the differences observed. In the latter case, the inlet and outlet lines for the reactor were heated to below 700°F, and the temperature coefficients for reaction determined from the literature indicate that reaction in these zones should be 500 to 1,000 times slower than at 1000°F and, therefore, negligible.

Effect of Temperature, H_2S and S Concentrations on the Heterogeneous Reaction To Form H_2S with - a Catalyst of Activated Carbon

The heterogeneous reaction was carried out in an identical reactor tube containing a small bed of activated carbon sized to approximate the gas residence time used in 4" pilot H_2S generation work. The rate of formation of H_2S in the bed was taken as the difference between the total H_2S production from the catalytic reactor and that found for the homogeneous reaction. At 1000°F where a considerable amount of H_2S was formed by homogeneous reaction, this treatment may not be completely accurate but the present results are at least illustrative.

The rates of H_2S formation found were 1.5 lb. mole/hr./ft.^{3} for Run I and 1.9 lb. mol/hr./ft.^{3} for Run II under the conditions listed in Table 47.

Table 49. COMPARISON OF HOMOGENEOUS AND HETEROGENEOUS REACTION RATES FOR SIMILAR INLET CONCENTRATIONS

	Rate H_2S Formation (lb. mol/hr./ft.^{3})	
	Run I	Run II
Homogeneous	0.029	0.025
Heterogeneous	1.5	1.9

A comparison to the homogeneous reaction may be made by calculating the homogeneous rate at the reactant concentrations corresponding to those at the inlet to the carbon bed which is located near the exit of the reactor tube assuming rate = $5100[S]^{1/2}[H_2]$.

It is seen, therefore, that the H_2S production rate increased 50 - 75 times in the presence of carbon. However, from these data it is still not clear whether the carbon has any particular catalytic influence. For example, the surface area of the reactor tube is approximately equal to the external area of the carbon particles in the reactor, so that on the basis of H_2S formed per unit of exposed surface, the "catalytic" rate is no more than twice the "homogeneous" rate. In spite of this, it still will be possible to obtain rates applicable to reactions within a carbon bed as employed in practice. It should be noted that the sulfur concentrations influent to the carbon in these experiments are equivalent to the equilibrium concentration over carbon containing adsorbed sulfur in the 10 - 11 lbs. S/100 lbs. C loading range. Such concentrations should be typical of vapor phase sulfur obtained during H_2S generation after most of the sulfur has been stripped off thermally.

Following the initial experiments a second set of experiments was performed to further compare the homogeneous and heterogeneous reactions, test the applicability of the sample rate expression $r_{H_2S} = k[H_2][S]^{1/2}$ and determine the effect of temperature on reaction rates. Table 50 lists the experimental conditions used. It is noted that in the case of the heterogeneous reaction, reactant concentrations influent to the carbon bed were assumed to be equal to the effluent concentration from the empty reactor. These were calculated based on the observed conversion in the homogeneous reaction.

The experimental data was treated by calculating, for each run, the values of the rate constant k from the observed rate of production of H_2S, the rate equation $r_{H_2S} = k[H][S_1]^{1/2}$ and the calculated averages of the hydrogen and sulfur concentrations between inlet and outlet. This implies differential conditions at the average concentrations, which is not entirely accurate.

If the assumed rate equation is valid, values of k should be equal at a given temperature and ln k should change linearly with 1/T. Table 51 shows the values of average

Table 50. EXPERIMENTAL CONDITIONS FOR SERIES HS-2

Uniform Conditions

Carbon Type:	WV-W Loaded to 24% S Run H
Bed Depth:	0.2 inches
Linear Veloc. at Exper. Temp.:	0.22 ft./sec.
Empty Reactor Volume:	0.00273 $ft.^3$
Carbon Bed Volume:	0.0000908 $ft.^3$
Carbon Weight:	2.255 grams

Temperatures and Concentrations

Conditions	Run						
	1	2	3	4	5	6	7
Temperature, °F	900	900	1000	1000	1000	1100	1100
HOMOGENEOUS REACTION							
% H_2 Inlet Conc.	30.1	20.0	30.1	20.1	30.2	30.0	19.9
% S_1 Inlet Conc.	10.0	10.0	10.1	10.1	14.5	9.93	9.93
HETEROGENEOUS REACTION							
% H_2 Inlet Conc.	28.7	19.0	26.6	17.4	25.7	23.2	14.0
% S_1 Inlet Conc.	8.29	8.84	5.73	7.07	9.07	1.20	3.35

Table 51. COMPARISON OF RATE CONSTANTS AT DIFFERENT TEMPERATURES

Run No.	Temperature, °F	k_{avg} (Hom.) x10^{-3}	k_{avg} (Het.) x10^{-3}
1	900	2.07	124
2	900	2.05	92
3	1000	5.40	309
4	1000	5.45	340
5	1000	5.68	340
6	1100	12.2	1,040
7	1100	15.1	810

k calculated for each of the runs made in the homogeneous and heterogeneous reactors. Agreement between values of k tends to support the assumption of the rate equation for both homogeneous and heterogeneous cases.

Figure 64 shows plots of ln k vs. 1/T for these data and compares the results of these experiments with those extrapolated from calculations based on the work of Norrish and Rideal, and Aynsley, et al. The experimental data is seen to yield straight line plots, the slopes of which are approximately equal for both the homogeneous and heterogeneous reactions. Activation energies calculated from these slopes are 40.9 Kcal for the homogeneous case and 44.7 Kcal for the heterogeneous reaction. The similarity of these activation energies indicates that while the presence of carbon apparently increases the reaction rate per unit volume of reactor, carbon does not have a specific catalytic effect, except perhaps by virtue of its surface area. Table 52 compares experimental reaction rates and rate constants based on the reactor tube surface area in the homogeneous case and the external carbon surface area in the heterogeneous case. This latter area was estimated as the surface area of spheres having the mean particle diameter of the carbon sample. On this basis the rate constant for the "heterogeneous" reaction was only about twice that for the "homogeneous" reaction. This is probably within the error of the external particle surface area estimate.

It may also be reactor surface area which accounts for the wide difference in results for the two literature investigations noted. In any case it is apparent that one aspect of future investigations must be to establish the proper reactor size basis for rate constant calculations.

Effect of Mass Transfer on H_2S Generation Kinetics -

Following H_2S generation experiments reported previously, the experimental program has continued to investigate: 1) "homogeneous" reaction kinetics with integral analysis of data, 2) gas film resistance and the effect of linear velocity on reaction over activated carbon.

Homogeneous Reaction - Empty Reactor -

Analysis of earlier experimental data was made assuming that differential reaction conditions were present but it was realized at the time that this could not be true since conversion of sulfur was in some cases almost complete. These data did, however, indicate that the rate expression

Figure 64. Arrhenius plots for experimental and literature data

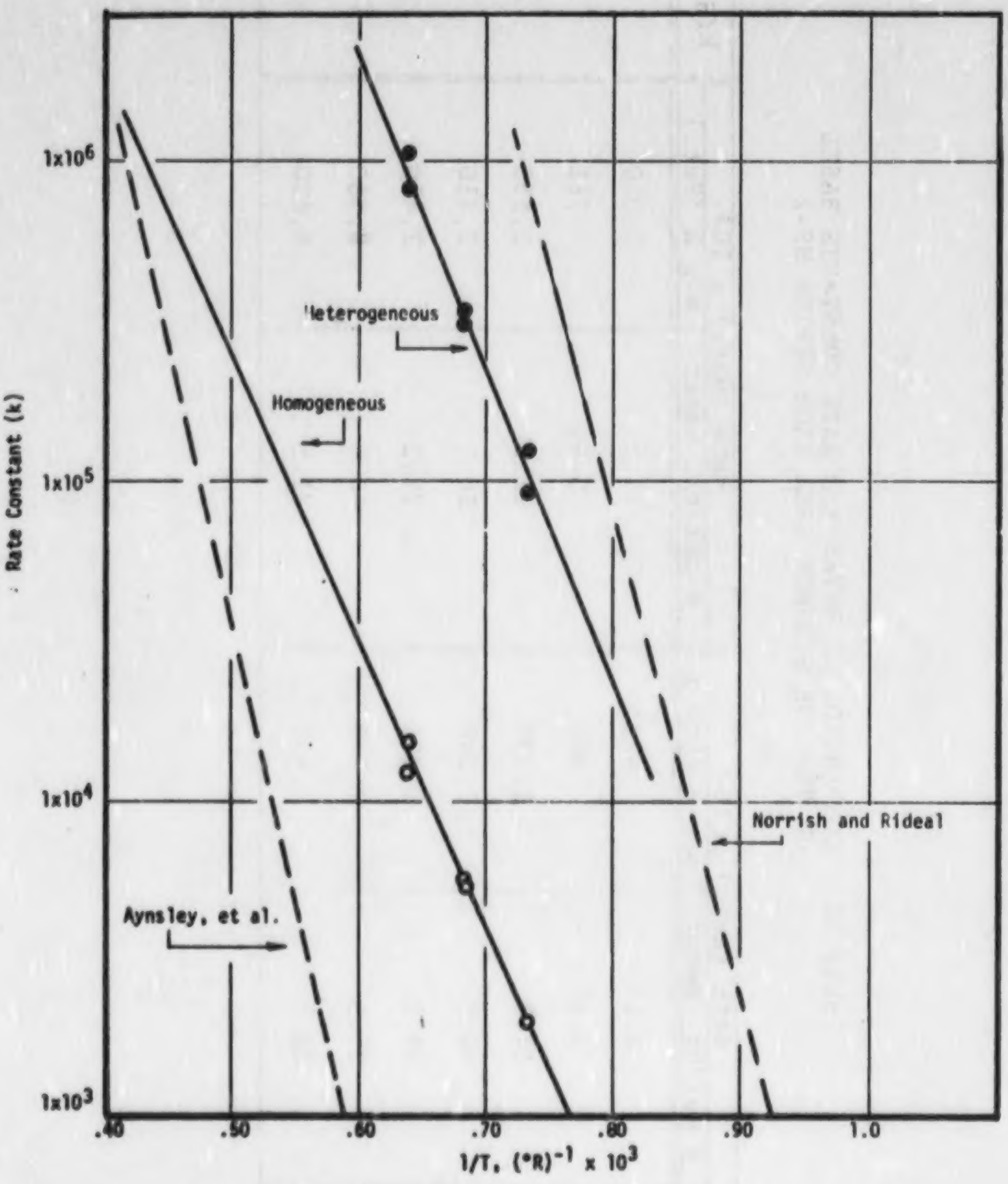


Table 52. COMPARISON OF RATES AND RATE CONSTANTS BASED ON REACTOR SURFACE AREA FROM SERIES HS-2

Run No.	Rate (Hom.) x 10^3		Rate (Het.) x 10^3		$k(Hom)/k_{Het}$
	# mol/hr. meter^2	avg k (Hom.)	# mol/hr. meter^2	avg k (Het.)	
1	6.14	470	11.2	1,020	2.17
2	4.10	466	5.91	761	1.63
3	14.3	1,230	21.2	2,550	2.07
4	10.0	1,240	16.1	2,810	2.27
5	18.2	1,290	27.2	2,810	2.18
6	25.5	2,770	26.6	8,560	3.09
7	22.1	3,450	21.8	6,690	1.94

$$r_{H2S} = k[H_2][S]^{1/2} \quad (51)$$

was likely candidate for further tests. To this end, the plug flow equation was integrated using an analogous rate expression as follows.

Derivation of Integrated Rate Equation -

Assuming reaction

$$H_2 + 1/2\ S_2 \longrightarrow H_2S \quad (52)$$

then:

$$N_{H2} = (N_{H2})_o - (N_{H2})_o X_{H2} \quad (53)$$

where N = moles reactant
N_o = initial moles reactant

$$N_{S2} = (N_{S2})_o - 1/2(N_{H2})_o X_{H2} \quad (54)$$

where X = conversion of reaction.

Assuming the rate expression

$$-r_{H2} = K\ C_{H2}\ C_{S2}^{1/2} \quad (55)$$

where C = concentration.

Dividing (54) and (55) by V, and substituting:

$$-r_H = K[C_H(1 - X_H)]\cdot[C_S - 1/2\ C_H X_H]^{1/2} \, * \qquad (56)$$

Assuming the plug flow equation

$$\frac{V}{(F_H)_o} = \int_o^{X_H} \frac{dX_H}{-r_H} \qquad (57)$$

where $(F)_o$ = initial molar flow rate
V = reactor volume

and substituting for r_H

$$\frac{V}{(F_H)_o} = \frac{1}{K}\int_o^{X_H} \frac{dX_H}{(C_H - C_H X_H)(C_S - 1/2\ C_H X_H)^{1/2}} \qquad (58)$$

This is integral of form

$$\int \frac{dX}{v\sqrt{u}} \qquad (59)$$

where $u = a + bx$, $a = C_S$, $b = -1/2\ C_H$
$v = C + dx$, $c = C_H$, $d = -C_H$
$k = ad - bc = C_H^2/2 - C_H C_S$.

Because for present data $C_H > 2\ C_S$, $kd < o$, therefore, proper integrated form is

$$\int \frac{dX}{v\sqrt{u}} = \frac{2}{\sqrt{-kd}} \arctan \left[\frac{d\sqrt{u}}{\sqrt{-kd}}\right] \qquad (60)$$

$$= \frac{2}{\sqrt{kC_H}} \arctan \frac{-C_H\sqrt{C_S - 1/2\ C_H X_H}}{\sqrt{kC_H}}\Bigg|_o^{X_H}$$

---

*Subscript molecular numbers are dropped, $H = H_2$ etc.

$$= \frac{2}{\sqrt{kC_H}} \left[\left(-\arctan \frac{C_H \sqrt{C_S - 1/2\ C_H X_H}}{\sqrt{kC_H}} \right) - \left(-\arctan \frac{C_H \sqrt{C_S}}{\sqrt{kC_H}} \right) \right]$$

$$= \frac{2}{\sqrt{kC_H}} (\arctan B - \arctan A)$$

where $B = C_H \sqrt{C_S} / \sqrt{kC_H}$

$A = C_H \sqrt{C_S / - 1/2\ C_H X_H} / \sqrt{kC_H}$

Then

$$\frac{V}{(F_H)_o} = \frac{2}{K\sqrt{kC_H}} \arctan \left(\frac{B - A}{1 + AB} \right) = \frac{Z}{K} \qquad (61)$$

where K = rate constant

$k = C_H^2/2 - C_H C_S$

$A = C_H \sqrt{C_S - 1/2\ C_H X_H} / \sqrt{kC_H}$

$B = C_H \sqrt{C_S} / \sqrt{kC_H}$

Confirmation of the integrated rate equation, (61), is obtained if the experimental data plotted as $V(F_{H2})_o$ vs. the right hand expression (Z) gives a straight line passing through the origin. The reaction rate constant can then be calculated from the slope of this line.

Experimental -

Experiments using the empty reactor tubes have now shown that the equation does properly describe the experimental results. In the course of these runs, however, it was discovered that the two matched reactor tubes, one of which was to be used for the reaction over carbon and the other which was to be left empty for reference did not produce the same conversion when both were run empty. Nevertheless the data obtained allowed testing of the proposed integrated rate equation.

Experimental conditions were:

Temperature: 1000°F

Sulfur Conc.: 15% as S_1

Hydrogen Conc.: 30% H_2

Reactor Volume: 0.00273 $ft.^3$ without inserts
0.00176 $ft.^3$ with inserts.

The results are shown in Figure 65. Run HS-3 was for the empty reference reactor and Run HS-4 was made using the empty reference reactor and the empty carbon reactor, both with Vycor inserts. This figure illustrates three findings:

1) The lines are straight and pass through the origin, indicating a correct rate equation.
2) There is a pronounced difference in the rates obtained using the reference reactor as compared to the empty carbon reactor although they have the same internal dimensions.
3) There is almost coincidence between the data taken with the reference reactor with and without the Vycor insert.

It is noted that this coincidence is related to using reactor volume at the reactor size factor in the term $V/(F_{H_2})_o$. Figure 66 shows that agreement is not as good if the reactor size factor is in terms of internal surface area, A, instead of volume, V.

With regard to the results of experiments in the reference reactors it would be tempting to conclude that there was relatively little contribution to reaction due to wall area and that a simple homogeneous rate constant could be best derived based on reactor volume. Yet the other reactor tube used in Run HS-4 which was dimensionally identical to the reference tube produced a significantly lower rate of reaction. Comparative reaction rate constants based on volume for the tubes are as follows:

Figure 65. Test of integral rate equation (61), Z as function of tube volume (Runs HS-3 and -4 reference reactor)

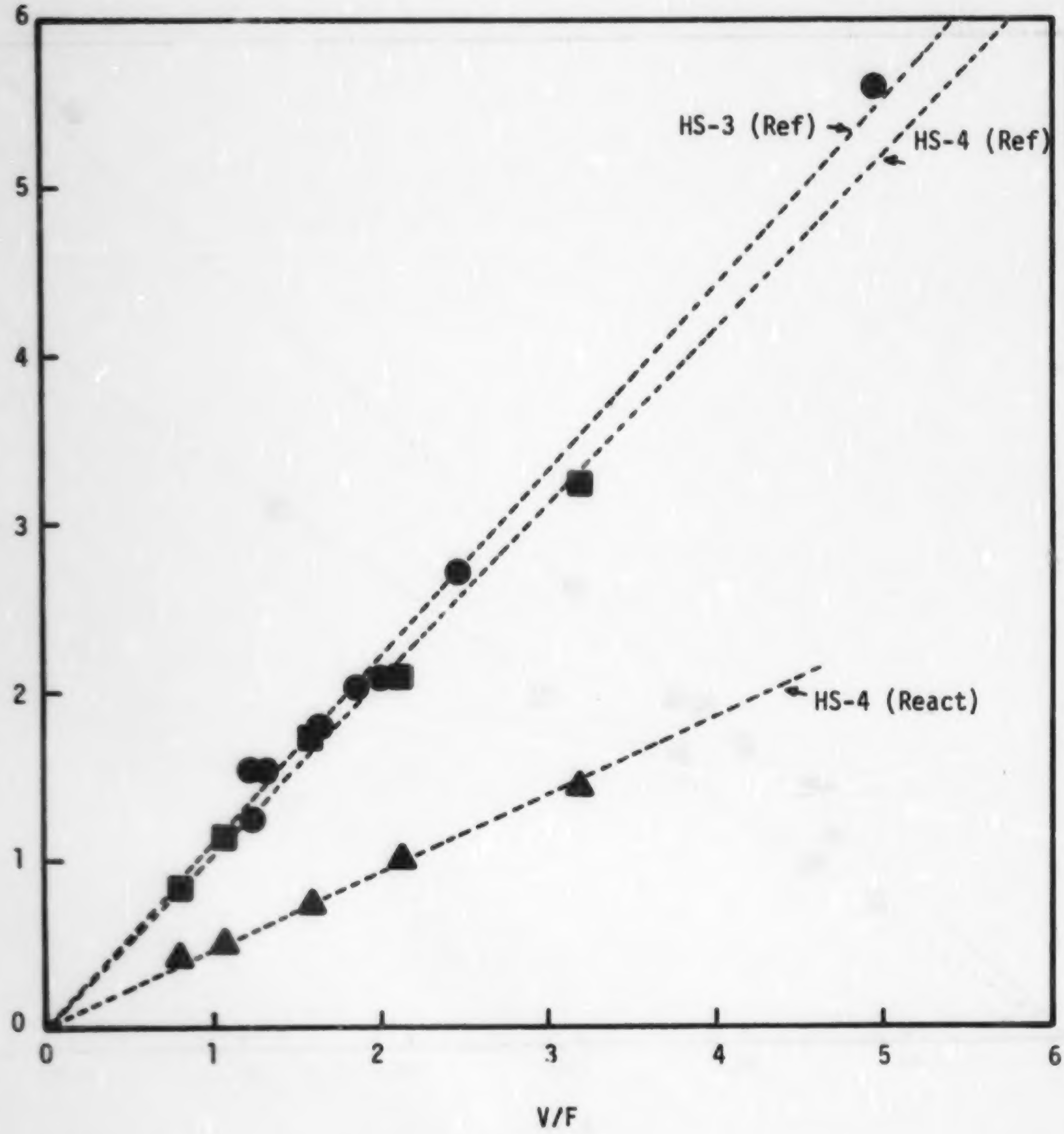
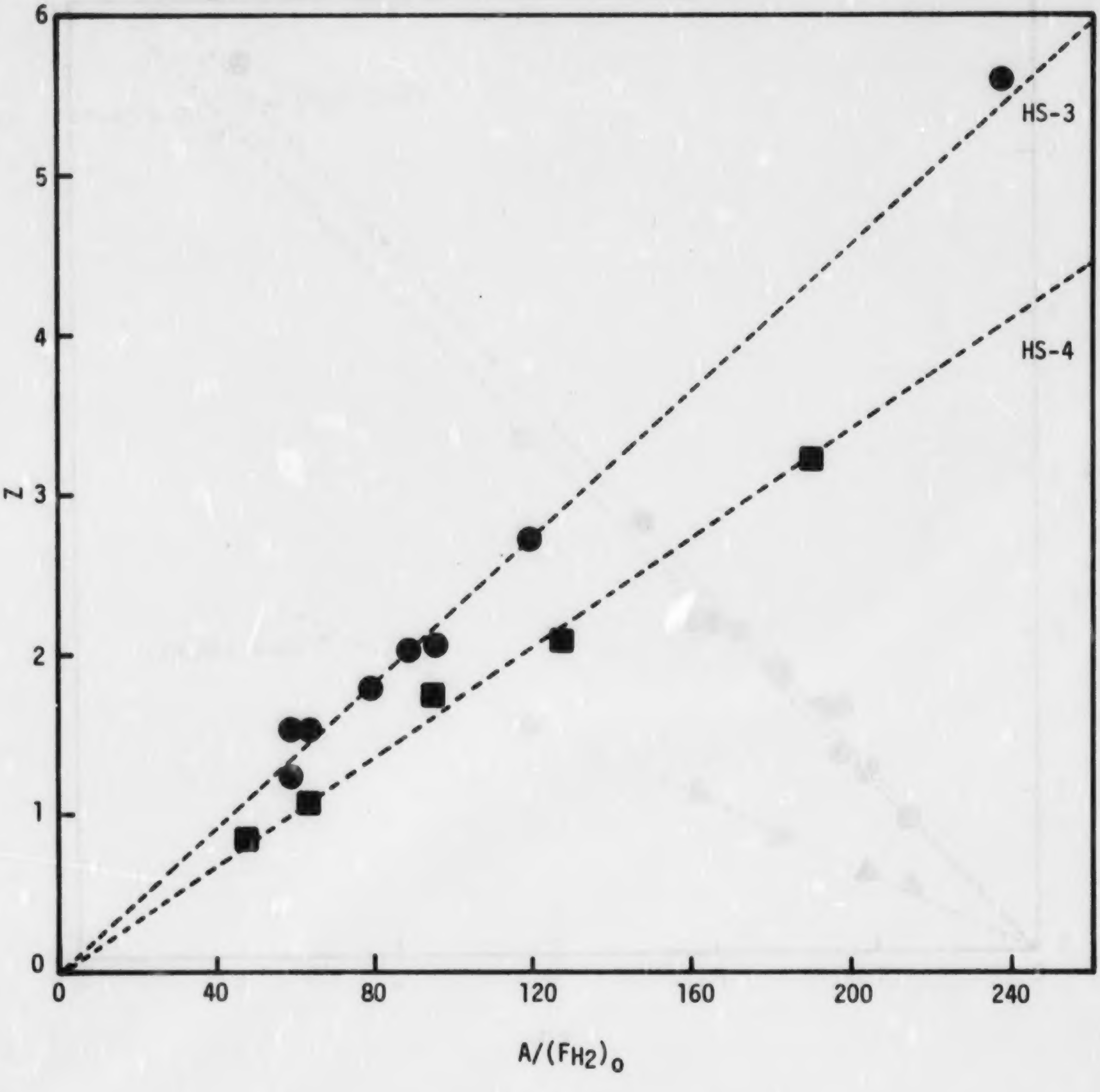


Figure 66. Test of integral rate equation (61), Z as function of tube area (Runs HS-3 and -4 reference reactor)



Run	Reference Tube	Carbon Tube
HS-3	11.0×10^3	---
HS-4	10.4×10^3	4.60×10^3

Whatever other conclusions are drawn from this, it is obvious that in studies of the reaction over carbon, it is not possible to account for the "homogeneous" contribution to total conversion using parallel data taken with this reference tube. Thus, the only alternative is to account for homogeneous reaction by means of the empty tube data for the reactor to be used in experiments with carbon.

Investigation of Mass Transfer Effects -

In the heterogenous reaction over carbon, the rate constant derived from bench scale data is to be applied to the pilot fluid bed case. Since there is a significant difference in gas linear velocity in the two cases it becomes necessary to determine the extent of velocity dependence, since such a dependence indicates a rate limiting resistance due to the diffusion rate of reactants and products through the gas film surrounding the carbon particles. An investigation was made by measuring conversion of hydrogen as a function of gas flow rate for three different carbon bed sizes. Experimental conditions are as noted in Table 53.

Table 53. EXPERIMENTAL CONDITIONS
FOR RUNS HS-4 TO HS-7

Carbon Type:	SG-32, 24% S Loading
Temperature:	1000°F
Inlet H_2 Concentration:	30%
Inlet S_1 Concentration:	15%
Carbon Bed Weights:	0, 1, 2, 4 gms
Carbon Bed Volumes:	0, 4.58×10^{-5}, 9.16×10^{-5}, 18.3×10^{-5} ft.^{3}
Total Gas Flow Rates:	1.96 to 7.84 ft.^{3}/hr. @ 1000°F
Space Velocity Range:	10,700 to 171,000 hr.$^{-1}$ @ 1000°F
Linear Velocity Range:	0.173 to 0.692 ft./sec.

The results of these experiments are shown in Figures 67 and 68. Figure 67 shows conversion of $H_2 (X_{H_2})$ as a function of bed volume/H_2 feed rate $[V/(F_{H_2})_o]$. If gas film diffusion were unimportant the data should all lie on a single curve. It is obvious that this is not the case here and that this resistance affected reaction rates at all velocities used. Figure 68 shows the conversion as a function of gas flow rate for nearly constant inlet conditions and space velocity. In the absence of film resistance, conversion would be constant with increasing linear velocity. Since the conversion continually increases, it is clear that these data are affected by mass transfer effects.

H_2S Generation Kinetic Model -

The kinetics of H_2S generation from the reaction of hydrogen and sulfur vapor over a catalyst of activated carbon have been studied. The effects on the reaction rate of H_2S formation, of temperature, of hydrogen concentration, of sulfur vapor concentration, and of mass transfer effects have been measured. This has led to a combination of all the variables into a kinetic model relating these variables to the rate of H_2S formation as given by Equation (62):

$$r_{H_2S} = k\, e^{-30645/T} (S_1)^{1/2} (H_2) \tag{62}$$

where r_{H_2S} = rate of H_2S formation, moles/hr.-m^2 of C surface area

$$k = \frac{2.08(10^9)(v)^{0.5}}{(299)(T)(e^{-30645/T}) + (v)^{0.5}},$$

moles/hr./m^2 of C surface area.

5.2.5 Combined Sulfur Stripping/H_2S Generation

The existing 8 stage, 4" diameter reactor was shown to be suitable for integral operation as a combined H_2S generator/sulfur stripper. The conclusion is based on the facts that 86% of the stripped sulfur was converted to H_2S (75% required), 81% of the H_2 was converted to H_2S (90% required), and the SO_2 activity of the carbon was 106% of the virgin precursor. Although 81% of the H_2 was converted to H_2S, 94% of the inlet H_2 was utilized. The unaccounted for H_2 was postulated as being chemisorbed onto the carbon or reacted with chemisorbed oxygen.

Figure 67. Variation of conversion with residence time for three bed volumes

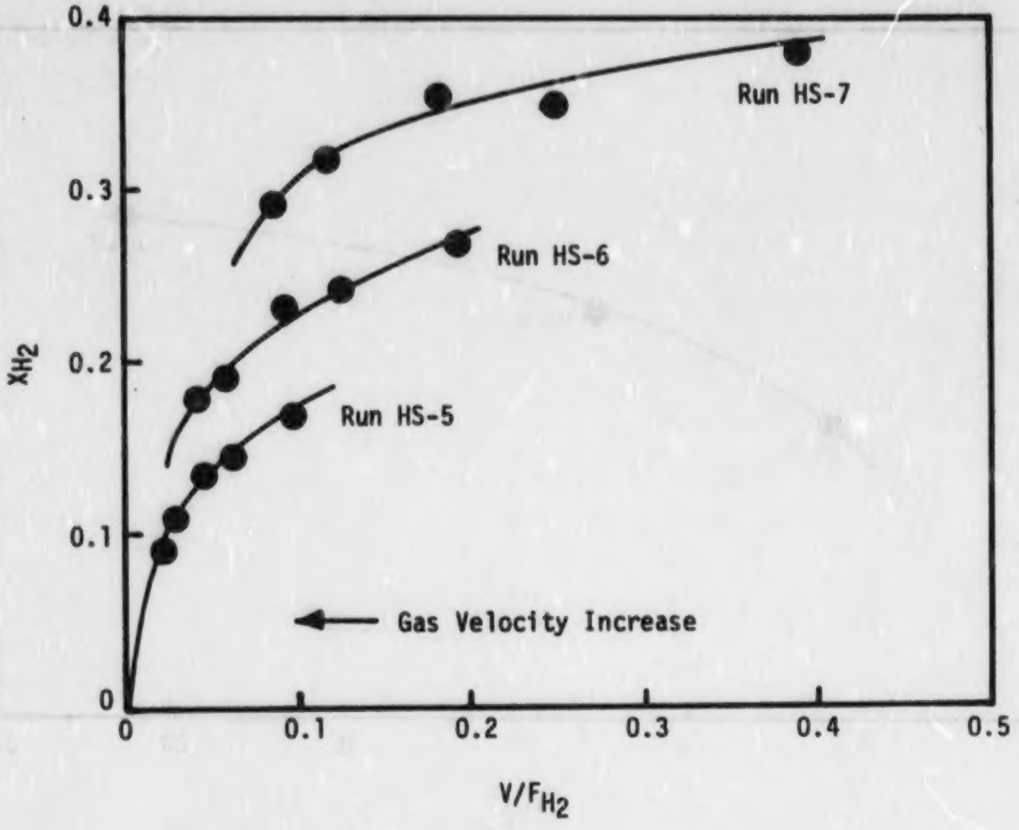
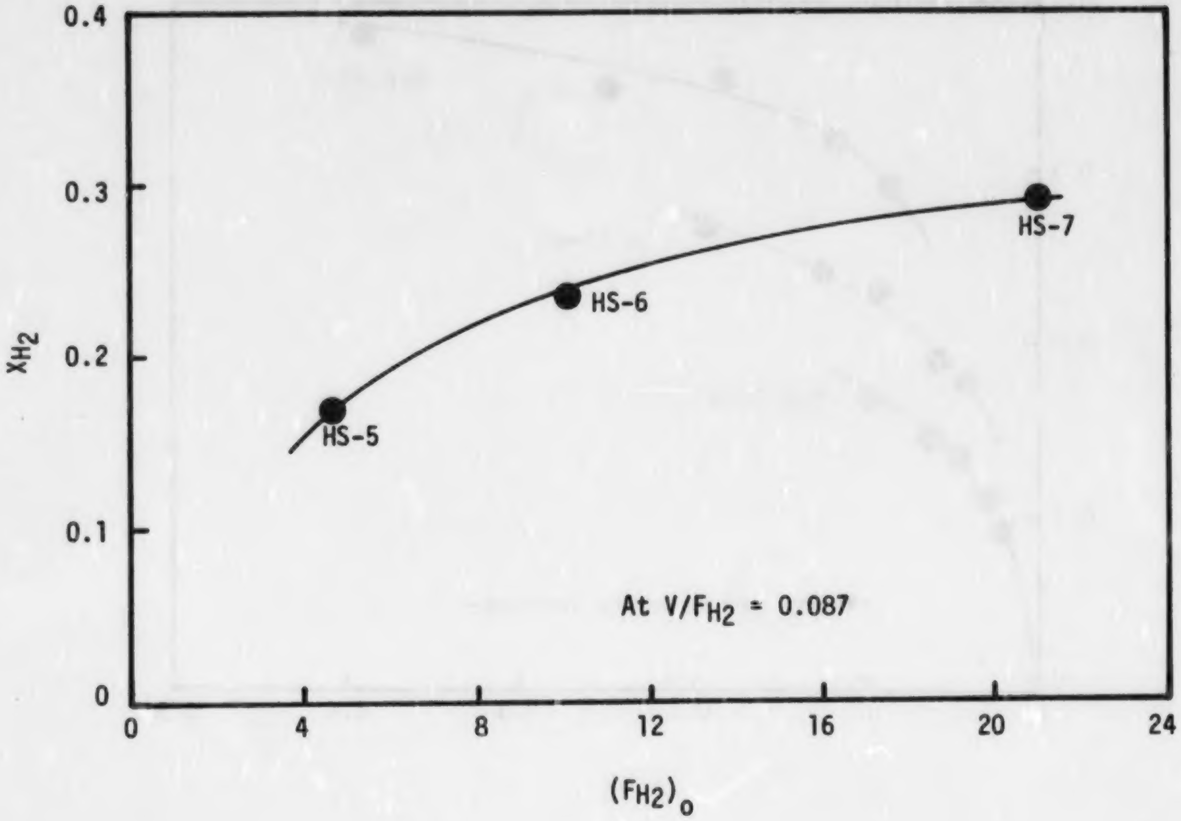


Figure 68. Effect of flow rate on conversion at constant residence time



Preliminary experiments suggested that the gas/solid contact time for the H_2/sulfur reaction should be increased. This equipment change was made, problems encountered in the initial runs were rectified, and the above mentioned objectives were met.

The overall results indicated that for sufficient sulfur removal, for carbon regeneration for SO_2 pickup, and for H_2/sulfur conversion to H_2S, the operating temperature would be 1000 to 1200°F, the inlet H_2 concentration would be 20 to 40 volume %, and the carbon residence times of 6 to 13 minutes were sufficient.

It was recommended that the 8 stage, 4" diameter regenerator be used in integral operation as a combined H_2S generator/sulfur stripper and be integrated with the 18"Ø SO_2 sorber. It was further recommended that runs be made on bench scale to verify the phenomena of H_2 chemisorption and that additional runs in the 4"Ø unit be considered to evaluate lower operating temperatures. The unit was used as a combined reactor in integrated operation with the 18"Ø SO_2 sorber. Also, some preliminary bench scale work on H_2 chemisorption was completed, as discussed in a previous section.

Combined Regeneration Process Concept -

In the Westvaco Process, SO_2 is removed from the flue gas by activated carbon. During the removal, SO_2 is converted to sulfuric acid which remains as the sorbed species on the outlet carbon. The sorbed acid is subsequently converted to elemental sulfur by the reaction with hydrogen sulfide. The next step is to recover one-fourth of the sulfur as elemental sulfur and the remaining three-fourths as hydrogen sulfide by reaction with hydrogen by Reactions 63 and 64:

$$4\ S\ (\text{Sorbed}) \xrightarrow[\text{Carbon}]{\text{Activated}} S + 3\ S\ (\text{Sorbed}) \qquad (63)$$

$$3\ H_2 + 3\ S\ (\text{Sorbed}) \xrightarrow[\text{Carbon}]{\text{Activated}} 3\ H_2S \qquad (64)$$

The hydrogen sulfide produced is used in the first step of regeneration. The reactivated carbon is recycled to the SO_2 sorber.

Results and Discussion -

For integral operation, both regeneration steps of sulfur stripping and H_2S generation can be carried out in the existing 8 stage, 4" diameter regenerator. The objectives of the task were met with 86% of the stripped sulfur converted to H_2S, 94% utilization of the inlet hydrogen, and the SO_2 activity of the product was 6% higher than the virgin precursor.

The conversion of H_2 and sulfur to H_2S increases with increasing temperature and with decreasing space velocity (increasing gas/solid contact time). The SO_2 activity of the carbon and removal of sulfur from carbon increases with increased residence time of the carbon in the reactor and with increased temperature.

The experimental results for all runs made to evaluate combined sulfur stripping/H_2S generation are summarized in Tables 54, 55 and 56 with detailed data given in Appendix A-18. Tables 54 and 55 give the average measurements for the carbon and gas phase, respectively. Table 56 summarizes the major response variables calculated from the experimental data.

Effect of Temperature on Sulfur Removal from Carbon -

As the temperature increases, the vapor pressure of sulfur over carbon increases. The presence of hydrogen in the gas phase enhances the driving force for the sulfur removal, because of the reaction of the hydrogen with sulfur in the gas phase and in the pores of carbon. The effect of temperature on the removal of the sulfur from the carbon with H_2 present is given in Figure 69. As expected, as the temperature increased, the percentage of sulfur stripped from the carbon in the 8 stage reactor increased. An operating temperature of 1000 to 1200°F is indicated from the data to provide sufficient removal rates of sulfur.

Effect of H_2 concentration and Carbon Residence Time on Sulfur Removal from Carbon -

The effect of H_2 concentration and carbon residence time on sulfur removal from carbon at 1200°F is given in Figure 70. As the hydrogen concentration increases the sulfur removal increases as expected. Also as the carbon residence time increases the sulfur removal increases. Carbon residence times of 6 to 13 minutes for an inlet H_2 concentration of 20 to 40 vol. % appears sufficient at 1200°F to provide sufficient removal of sulfur.

Table 54. EXPERIMENTAL CONDITIONS FOR EVALUATION OF COMBINED SULFUR STRIPPING/H_2S GENERATION

Expt. Number	Carbon																
	Inlet			Carbon Residence Time minutes	Outlet			Cyclone		Temperature, °F							
										Stage Number							
	% S	Mat'l Rate #/hr.	C Rate #/hr.		% S	Mat'l Rate #/hr.	C Rate #/hr.	% S	Mat'l Rate #/hr.	# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8
SHG-1	20.70	40.5	32.2	10	15.79	37.3	31.4	28.9	0.0055	768	771	781	778	801	799	----	734
SHG-2	20.30	35.1	28.0	11	4.85	29.1	27.8	42.7	0.0036	942	970	982	967	1001	970	----	840
SHG-3	20.35	30.9	24.6	13	2.82	23.85	23.2	----	0.0033	1130	1168	1178	1147	1148	1115	----	914
SHG-5	19.78	30.9	24.8	13	4.91	25.1	23.9	----	----	1144	1169	1179	1140	1170	1139	----	951
SHG-7	20.16	30.9	24.7	13	2.80	25.0	24.3	----	----	1135	1175	1180	1192	1198	1025	----	910
SHG-8	5.08	25.2	23.9	13	2.90	24.9	24.2	----	----	1132	1168	1178	1150	1178	1178	----	938
SHG-9	20.12	30.9	24.7	13	2.64	24.6	24.0	----	----	1140	1173	1186	1165	1187	1164	----	918
SHG-10	19.81	35.0	28.1	10	4.21	28.9	27.7	25.4	0.015	1132	1135	1072	899	1120	1219	1024	----
SHG-11	19.81	35.0	28.1	10	8.27	30.8	28.2	31.2	0.021	1070	1035	1040	925	1085	1207	1170	----

Table 55. EXPERIMENTAL CONDITIONS FOR EVALUATION OF COMBINED SULFUR STRIPPING/H_2S GENERATION

Expt. Number	Gas												Temperature, °F								
	Inlet				Outlet								Stage Number								Avg.
	Linear Gas Velocity ft./sec.	Total Gas Flow, CFH A 70°F	H_2 Flow, CFH @ 70°F	H_2 Conc., Vol. %	Gas Concentration, Vol. %							Sulfur Conc. # S_1/hr.	# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	
					H_2	H_2S	SO_2	H_2O	CO	CO_2	N_2										
SHG-1	1.9	254	66	26.8	16.2	4.1	0.20	6.30	0	1.0	68.3		800	----	800	----	806	----	801	----	802
SHG-2	2.0	229	67	32.0	10.0	13.4	0	8.50	0	1.25	68.5		997	----	997	----	997	----	990	----	995
SHG-3	1.9	191	52	29.8	3.1	15.2	0	5.90	0	1.80	70.7		1203	----	1200	----	1205	----	1192	----	1200
SHG-5	2.1	214	22	5.4	0	3.0	0.07	5.40	0	1.40	88.0		1212	----	1204	----	1208	----	1201	----	1206
SHG-7	1.8	176	63	37.7	5.2	18.6	0	6.50	0	1.70	64.7		1210	----	1207	----	1222	----	1192	----	1208
SHG-8	1.8	176	63	36.7	27.7*	2.6	0	0.42	0.01	0	69.4		1210	----	1200	----	1210	----	1208	----	1207
SHG-9	2.0	202	53	27.3	3.06	13.0	0.007	5.73	0	1.40	71.7		1210	----	1195	----	1202	----	1197	----	1201
SHG-10	2.0	206	79	36.1	2.0	27.3	0	9.0	0	1.80	60.0		1215	1182	1198	992	1204	1234	1200	1248	1184
SHG-11	2.0	202	0	0	0	1.32	0.82	9.0	0	2.00	88.0		1200	1150	1150	1020	1135	1290	1215	1130	1161

*Used Stage 7 analysis (stage below gas outlet).

Table 56. EXPERIMENTAL RESULTS FROM EVALUATION OF COMBINED SULFUR STRIPPING/H_2S GENERATION

Expt. Number	Space Velocity, Vol. Gas/ Vol. C/ hr.	Hydrogen Balance In/Out	Sulfur Balance In/Out	# mole S Stripped/ hr.	# mole H_2 Avail.(H_2+S)/ hr.	# mole S Stripped/ # mole H_2 Available	Sulfur Stripped % of Inlet	* H_2 Utiliz. % of Inlet	** H_2 Conv. to H_2S, % of Inlet H_2	** S Conv. to H_2S, % of S Stripped	SO_2 Activity Rel. to Virgin Carbon
SHG-1	1,650	1.31		0.079	0.178	0.44	30	39	16	35	---
SHG-2	1,490	1.34		0.179	0.198	0.90	80	68	43	47	0.98
SHG-3	1,240	1.72		0.176	0.153	1.15	89	90	48	42	---
SHG-5	1,390	1.72		0.152	0.028	5.43	80	100	58	10	---
SHG-7	1,150	1.73		0.173	0.176	0.98	89	87	45	55	1.15****
SHG-8	1,150	1.32		0.017	0.170	0.10	44	18	7	64	---
SHG-9	1,320	1.80		0.174	0.145	1.20	90	89	45	38	---
SHG-10	1,530***	1.15	1.03	0.179	0.186	0.96	82	94	81	86	1.06
SHG-11	1,530	----		0.129	---	---	62	---	---	---	---

*Goal ≥90%.

**Goal ≥75%.

***Effective space velocity for H_2 + S reaction in vapor phase ≈3,000 $hr.^{-1}$.

****SO_2 activity of carbon sample from Stages 4 and 5 was about 0.94.

Figure 69. Effect of temperature on sulfur stripping with H_2 present

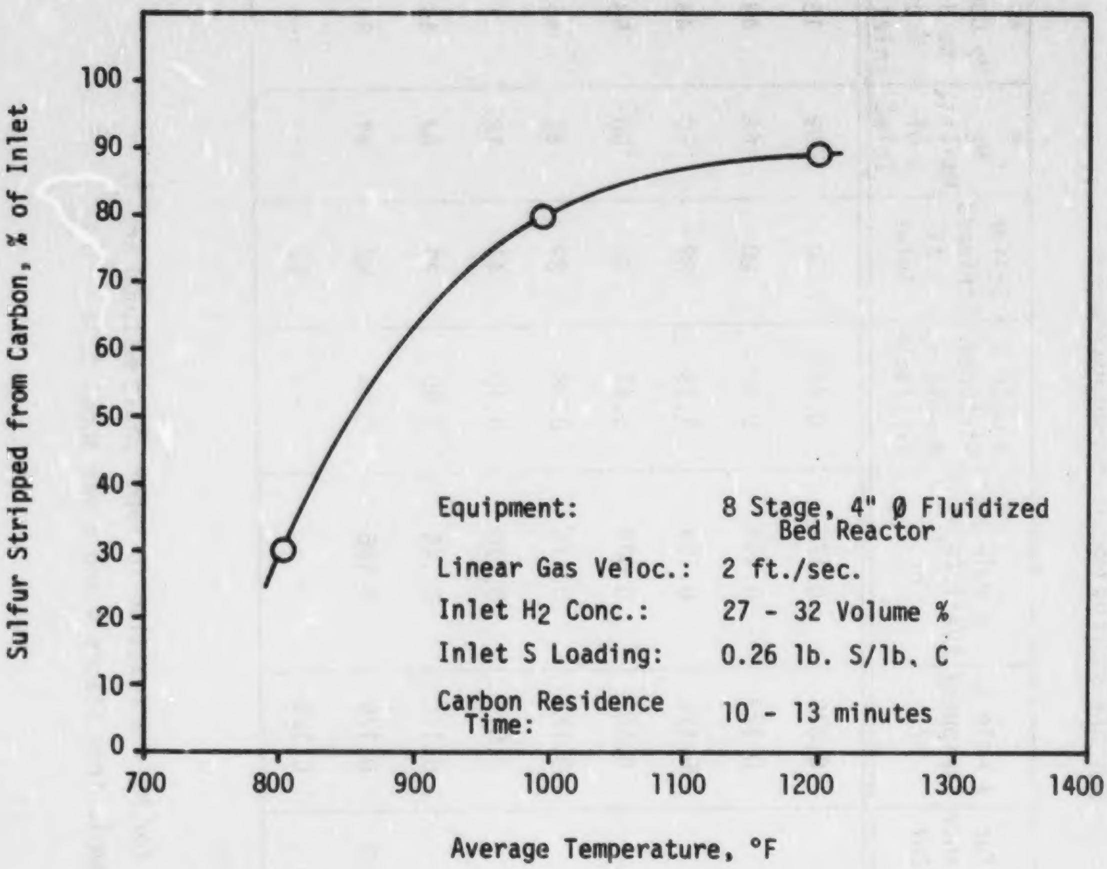
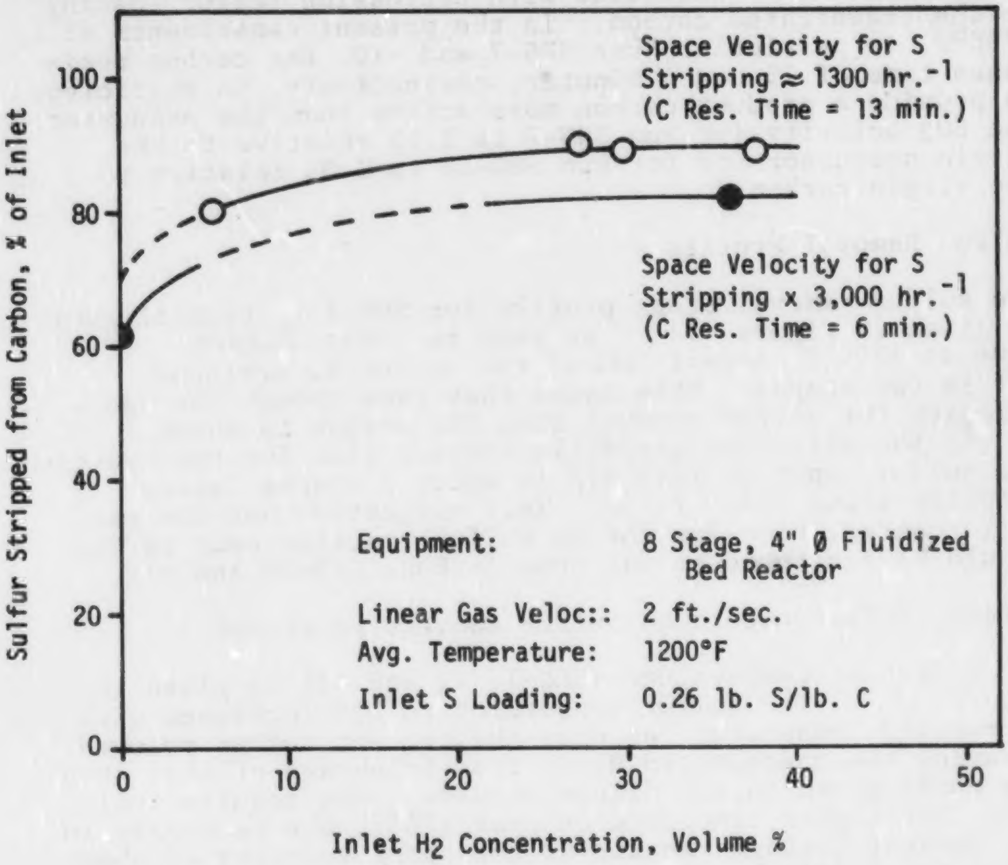


Figure 70. Effect of H_2 concentration and gas/solid contact time on sulfur stripping at 1200°F



Effect of Carbon Residence Time on SO_2 Activity -

From previous work, it is known that the SO_2 activity is a function of the final sulfur loading, regeneration temperature, and time of exposure to a reducing atmosphere. The SO_2 activity increases with increasing temperature and exposure time to a reducing atmosphere. At a fixed temperature the activity increases with decreasing sulfur loading on the regenerated carbon. In the present experiments at 1200°F, in particular Runs SHG-7 and -10, the carbon residence time of 13 and 6 minutes, respectively, is sufficient to provide a product carbon more active than the precursor. The SO_2 activity for Run SHG-7 is 1.15 relative to the virgin precursor and for Run SHG-10 is 1.06 relative to the virgin carbon.

Sulfur Removal Profile -

The sulfur removal stage profile for SHG-7 (a typical run) is given in Figure 71. As seen in this figure, made at 1200°F, almost all of the sulfur is stripped off in two stages. This means that even though the space velocity for sulfur removal from the carbon is about 1,150 $hr.^{-1}$, the effective gas/solid contact time for the hydrogen and sulfur vapor to form H_2S is about 2 stages (space velocity about 4600 $hr.^{-1}$). This suggested that the gas/solid contact time for the H_2 sulfur reaction over carbon should be increased, as was done in Runs SHG-10 and -11.

Effect of Temperature on Sulfur Conversion to H_2S -

The effect of temperature (SHG-1, -2 and -3) is given in Figure 72. The sulfur conversion to H_2S increases with increasing temperature, as does the percent sulfur removed. Assuming the unaccounted H_2 is from inleakage of air, then the curve given in the figure results. The results indicate that higher temperatures near 1200°F are necessary in the present 8 stage reactor at the space velocity of about 5,000 $hr.^{-1}$ for the H_2/sulfur reaction. In Run SHG-10 the space velocity for the H_2/sulfur reaction was decreased to about 3,000 $hr.^{-1}$ by feeding most of the carbon at the middle of the column. This increased the conversion of the sulfur to H_2S and indicates that the temperature may be decreased below 1200°F and still allow the goals to be met.

Carbon Burn-off Rate -

The CO_2 produced during the runs was necessarily indicative of carbon burn-off. Previous experiments indicated that first cycle burn-off could be as high as 92 lbs. C/Ton sorbed SO_2. Burn-off then appeared to decrease to as low

Figure 71. Sulfur removal from activated carbon in an 8 stage, 4" diameter regenerator

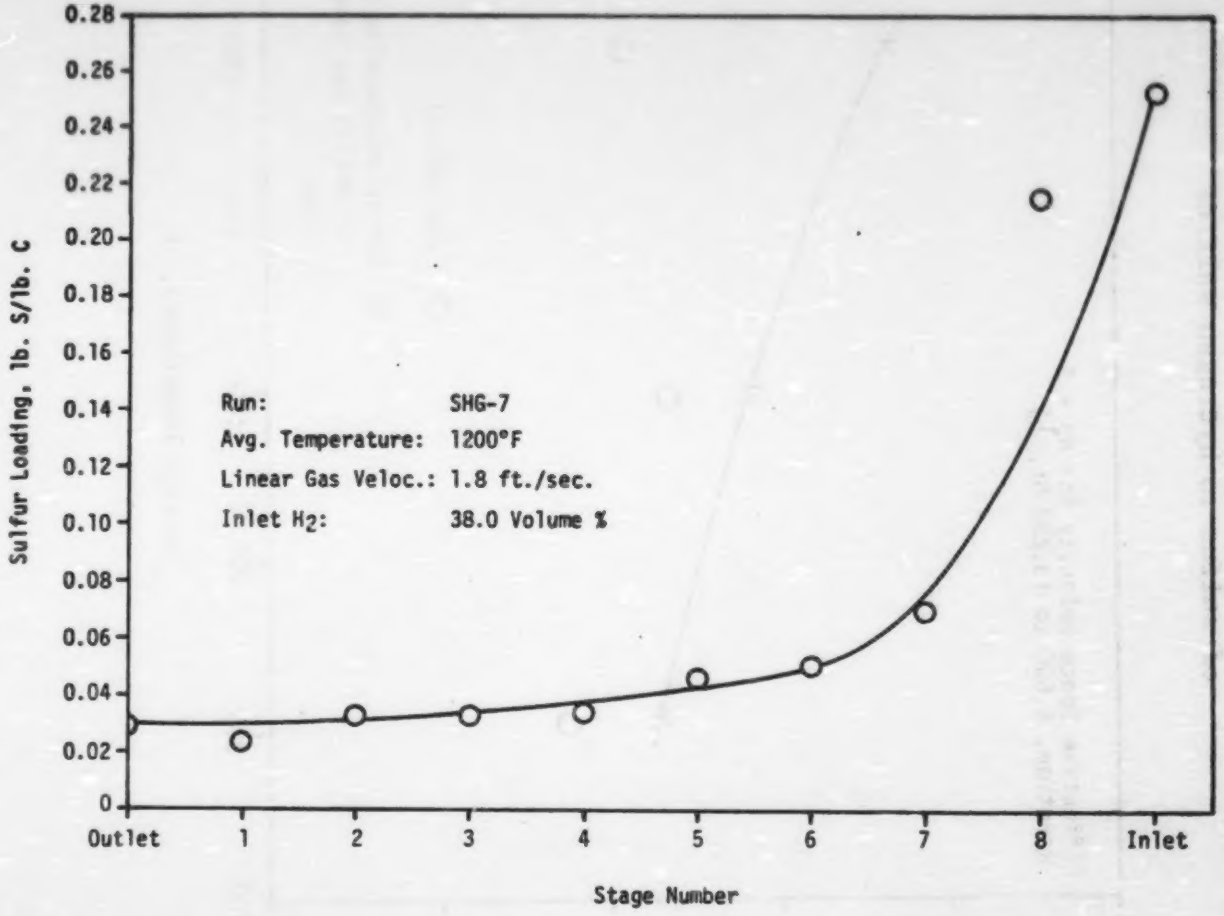
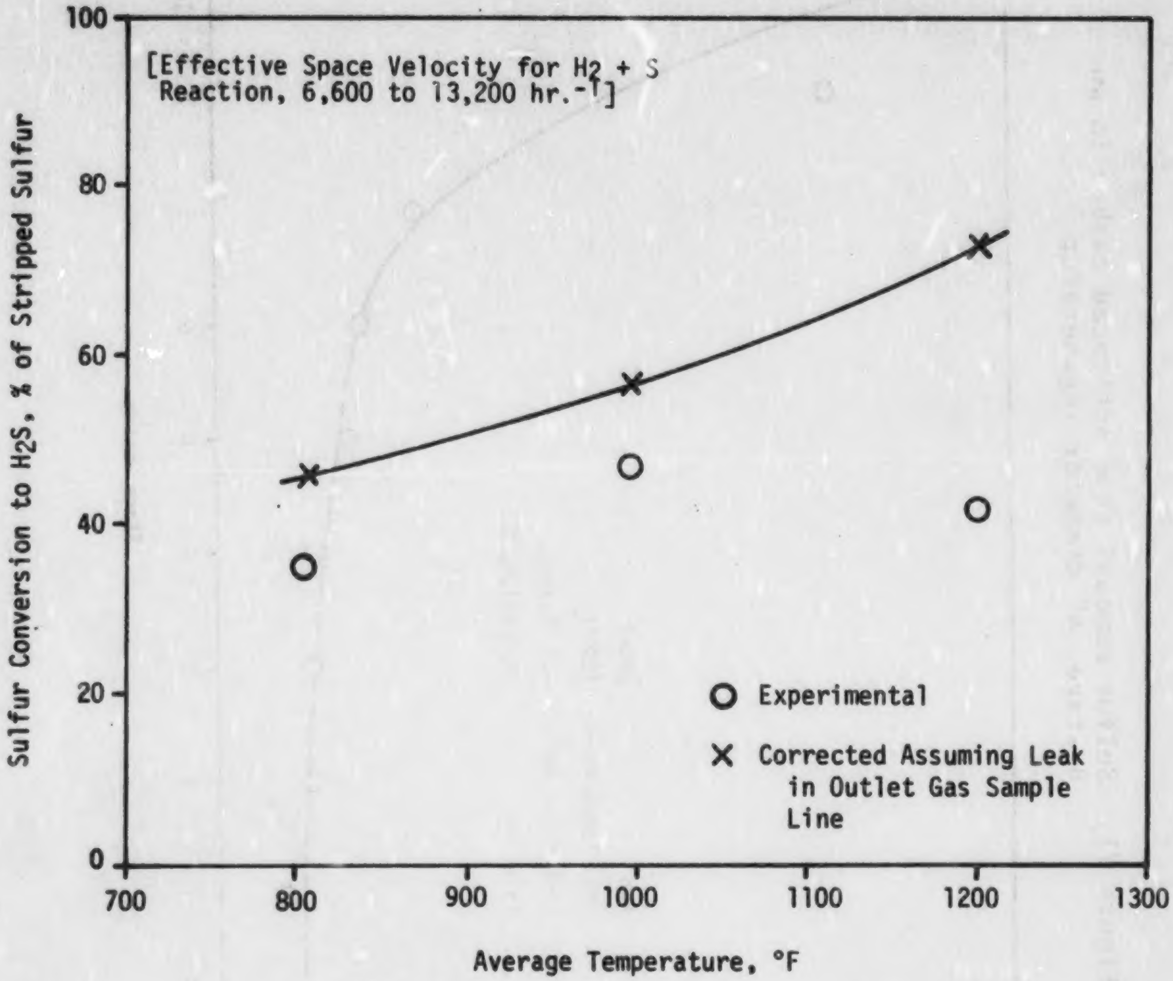


Figure 72. Effect of temperature on the conversion of sulfur to hydrogen sulfide



as 2 lbs. C/Ton SO_2 after 8 cycles. The data from Run SHG-10 (1.8 vol. % CO_2) was equivalent to a burn-off of 67 lbs. C/Ton sorbed SO_2 for a carbon loss of 0.42 wt. %. Recent experimental and literature studies indicate that oxygen may be chemisorbed on the carbon. This is then evolved as CO and CO_2 at elevated temperatures in the presence of oxygen-free gas. Since chemisorbed oxygen would be depleted as CO_2 is evolved, burn-off should decrease with cycling, as shown by the previous data.

Runs SHG-1 to -9 -

After Runs SHG-1 to -9 had been made a number of equipment problems were found and subsequently corrected. The first problem was a leak in the gas sample lines. A second problem was that the chromatographic gas analysis of hydrogen had been specified by the manufacturer to be linear, but the calibration was subsequently found to be non-linear. The hydrogen concentrations were adjusted accordingly with the resultant values given in Table 55.

For a typical run, SHG-7, to see the effect of the leak in the outlet gas line, if the assumption is made that all of the unaccounted H_2 was due to the inleakage of air into the outlet gas sample line, then the outlet H_2 and H_2S concentrations would be increased accordingly to 7.3 and 26.2 volume %, respectively, from 5.2 and 18.6 (see Table 55). This would then mean 81% conversion of the stripped sulfur to H_2S and 79% H_2 utilization; however, as discussed later, there is another factor affecting this assumption which increases the H_2 utilization to form H_2S. Also the source of the H_2O in the vapor phase will be discussed later.

Regardless of the problems encountered in these first runs, the data suggested that additional runs should be made to increase the gas/solid contact time (decrease space velocity) for the reaction of H_2 with sulfur and that 4 stages would be sufficient for the necessary sulfur removal.

Runs SHG-10 and -11 -

Therefore, the equipment was modified to allow the carbon to be fed both at the inlet and at Stage 4 (number from bottom to top). These runs (SHG-10 and -11) were made at 1200°F with 85% of the carbon fed to Stage 4 and 15% fed to Stage 7. This increased the effective number of stages for H_2 sulfur contact by three, but decreased the number for reactivation for SO_2 pickup by about four.

Run SHG-11, with only N_2 in the inlet gas, showed that the water in the gas phase came from water sorbed on the carbon. Subsequent moisture determinations in bench scale equipment verified the findings in this run. The water on the carbon probably came from sorption of H_2O from the air during handling.

In Run SHG-10, 86% of the stripped sulfur was converted to H_2S, 95% of the H_2 was utilized (81% converted to H_2S), and the outlet carbon had an SO_2 activity 6% higher than the virgin precursor. The discrepancy of H_2 utilization (94 vs. 81%) is tied up in the hydrogen material balance, namely 0.37 lb. H_2/hr. into the reactor and 0.32 lb. H_2/hr. out of the reactor. Based on literature data on O_2 and H_2 chemisorption[6,7,8] and work Westvaco has completed on O_2 chemisorption, it is felt that the unaccounted hydrogen is chemisorbed. Calculations show that only about 0.1 mole of H_2/100 gms. C would have to chemisorb on the carbon to account for the H_2. The literature data taken on similar activated carbonaceous material showed the chemisorption of O_2 and H_2 are similar on a mole/gram basis. This fact, combined with Westvaco data on O_2 chemisorption at 530°F of about 0.03 mole/100 gms. C with actual plant produced carbon containing about 0.1 mole O_2/100 gms. C, makes a strong case for the H_2 chemisorption as a possible mechanism for accounting for the H_2. The literature data indicates that once the H_2 is chemisorbed, then it is irreversible unless the temperature is increased to about 1800°F. This means the phenomena might be expected only in the first few cycles. If the H_2 chemisorption mechanism is accepted then the effective H_2 conversion for the formation of H_2S is increased to 94%. Loss of hydrogen by leakage in these runs is discounted, based on the fact that the sample lines were tested with known gases at the reaction temperature.

5.2.6 Elemental Sulfur Recovery

A sulfur condenser was required for operation of the integral pilot plant on a closed loop cycle using H_2S produced internally with the process. A condenser was designed, installed, and tested prior to use in the integral run. This pilot development of the condenser resulted in smooth operation of sulfur condensation and recovery during the integral operation. The pilot development and results for the sulfur condenser prior to the integral run are given below.

Sulfur Condenser Operation -

Initial Sulfur Condenser Testing -

Initial sulfur condenser tests were made without a recirculating stream of liquid sulfur for scrubbing purposes. These runs, discussed below, provided a basis for improved condenser design and operation. The run conditions for three initial runs that were made are summarized in Table 57.

Table 57. OPERATING CONDITIONS FOR SULFUR CONDENSER TESTING SYSTEM

Liquid Sulfur Reservoir Temperature - 290-300°F

Liquid Sulfur Reservoir Pressure - 2 - 5 PSIG

Liquid Sulfur Flow Rate to Vaporizer - 6 lbs./hr.

N_2 Carrier Flow Rate to Condenser - 225 SCFH

Sulfur Vaporizer Temperature - 1000-1200°F

Condenser Inlet Gas Temperature - 1000°F

Condenser Outlet Gas Temperature - 250°F

Condenser Steam Jacket Temperature - 250°F

Condenser Exit Gas Sample Flow Rate Through Trap - 2 - 3 SCFH

The results of running at these conditions are summarized in Table 58. The first run showed a 61% recovery of sulfur, i.e., of the sulfur which left the reservoir, 61% was recovered from the condenser as a liquid. The rest was carried out with the nitrogen off-gas. For the second and third runs a mist eliminator, consisting of a roll of

Table 58. SULFUR CONDENSER TEST RUNS

Run	Duration minutes	N_2 Flow Rate SCFH	Avg. Sulfur Flow Rate lbs./hr.	Flow Rate Range lbs./hr.	Avg. Sulfur Vapor Conc. lbs. S/lb. N_2	Recovery %
1	260	230	2.2	1 - 5	0.13	61
2	180	230	3.0	1 - 7	0.18	88
3	104	230	3.0	2.5 - 3.5	0.18	88

tightly wound wire mesh, was placed inside the condenser, increasing recovery to 88% in both subsequent runs. However, there is some question as to the validity of these percentages, because the possibility exists that some liquid sulfur may have bypassed the vaporizer; i.e., it may have passed through unvaporized and reached the condenser as a liquid. If this condition did exist, then the actual condenser efficiency would be lower than it appears.

In order to achieve 99% recovery of the sulfur, it was necessary to provide some degree of scrubbing action. One approach would be to circulate a stream of liquid sulfur through the condenser, as was originally intended when the condenser was designed. Another method would be to further process the off-gas by bubbling it through a column of liquid sulfur.

Sulfur Condenser Operating Results -

All of the experiments performed prior to integral testing on the recovery of sulfur from regeneration off-gases by condensation are summarized in Table 59. As can be seen from the data, the original baffled exchanger without sulfur recirculation or a mist eliminator removed about 61% of the desired sulfur. Addition of a mist eliminator increased recovery to 88%; however, it was found that the scrubbing action of recirculating liquid sulfur was necessary to raise sulfur recovery to the desired 99+%. Addition of 29% H_2S to the gas contacting the recirculating sulfur caused no apparent changes in sulfur viscosity, as indicated by the constant pump electrical load over a six hour period. The jacket cooling fluid was changed from steam to hot water to facilitate temperature control and improve heat transfer rates. The recirculating sulfur condenser system was

Table 59. SULFUR CONDENSER OPERATION

Run No.	Comments	Gas Composition, %			Total** Gas Flow, CFH @ 70°F	Sulfur Recirculation Rate, GPM	Jacket Coolant	Temperatures, °F				Run Time, hours	Sulfur Recovered, %	Off-Gas Sulfur Conc., mole %
		Sulfur*	H_2S	N_2				Jacket Inlet	Jacket Outlet	Cond. Inlet	Cond. Outlet			
1	Much S Vapor/Mist in Off Gas	18	0	82	164	0	Steam	280±10	290±10	1000±50	--	4.3	61	--
2	Installed Mist Eliminator	13	0	87	236	0	Steam	280±10	295±10	1000±50	--	3.0	88	--
3	Tried Unsuccessfully to analyze off gas S conc. Achieved better control of S flow to vaporizer. Experienced problem controlling jacket temp.	15	0	85	226	0	Steam	290±10	305±10	1000±50	316±5	1.7	88	--
4	Liquid S recirculation installed. Also new steam-life cooling system.	13	0	87	225	0.5	Water	270±5	270±5	890±30	280±10	4.0	99.6	0.08
5	Pump enclosed in heated box. Pump motor current constant @ 7.5 amps. Observed no change in liquid S viscosity.	0	29	71	231	0.5	Water	260±5	265±5	875	290±10	6.0	--	--

*As S_1.

**Based on Sulfur as $S_{6.5}$.

tested for 14 hours of intermittent operation without serious problems and was used as the basis for design of a system for installation in the pilot plant. Because of the unusual viscosity characteristics of sulfur, temperature control will be a major design consideration in order to keep all parts carrying liquid sulfur in the range 260-315°F.

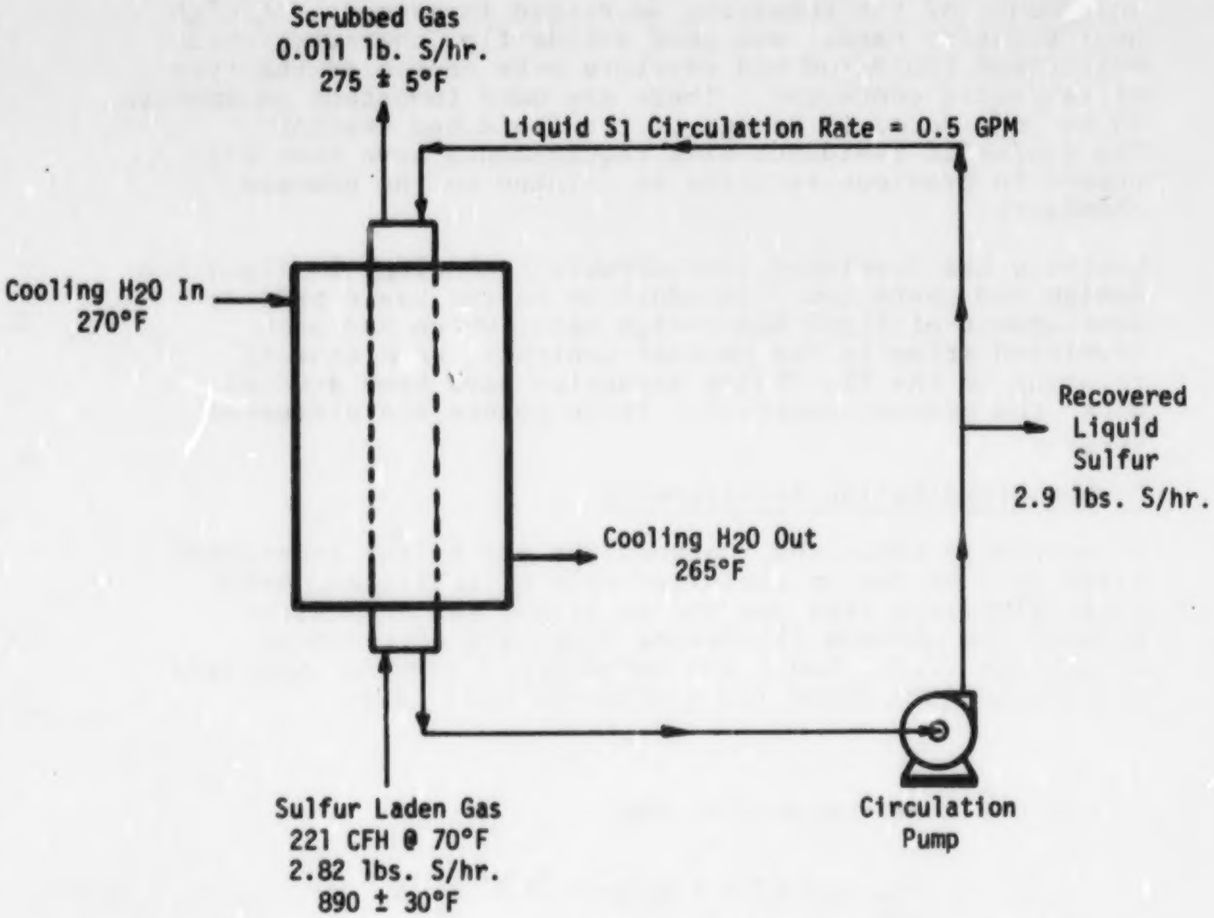
The feasibility was shown experimentally of a sulfur condenser system using recirculation of liquid sulfur as a scrubbing media. The anticipated improvement in the condensing efficiency to 99.6 weight % was realized.

The run conditions for the best sulfur performance are schematically shown in Figure 73. The sulfur concentration in the outlet gas from the condenser was determined by weight pickup by passing a slipstream through a tube packed with glass wool at room temperature. The slipstream volume was measured with a wet test meter. The sulfur on the glass wool was determined by extraction with carbon disulfide. The run, which lasted four hours, operated with an outlet gas concentration near equilibrium. From equilibrium the sulfur rate in the off-gas from the condenser is predicted to be 0 0088 and 0.0132 lb./hr. at 260 and 270°F, respectively. In the run made, the actual temperature was 275 ± 5°F with a sulfur rate of 0.011 lb. S/hr. measured. Even with a predicted accuracy of 50% for the off-gas sulfur concentration analysis, the condenser is operating near equilibrium conditions. The success of the run is strengthened by the material balance of 11.3 lbs. sulfur vaporized into the system over the four hour period and 11.7 lbs. sulfur recovered from the system in the outlet streams.

The safe lower operating outlet gas temperature is about 260°F because the liquid sulfur solidifies at 238°F and a safety margin of about 20°F is recommended. Although there were problems with the sulfur circulating pump during start-up, it functioned well during the run.

It has been demonstrated that the sulfur condenser can achieve the desired condensing efficiency of greater than 99%. The improved performance is the direct result of the liquid sulfur recirculation system, which provides the scrubbing action needed to condense the sulfur mist.

Figure 73. Operating conditions for sulfur condenser


Scrubbed Gas
0.011 lb. S/hr.
275 ± 5°F
Liquid S_1 Circulation Rate = 0.5 GPM
Cooling H_2O In
270°F
Recovered
Liquid
Sulfur
2.9 lbs. S/hr.
Cooling H_2O Out
265°F
Sulfur Laden Gas
221 CFH @ 70°F
2.82 lbs. S/hr.
890 ± 30°F
Circulation
Pump

SULFUR MATERIAL BALANCE

Sulfur In	- TOTAL IN	11.3 lbs.
Sulfur Out	- Liquid	11.7 lbs.
	- Gas	.04 lbs.
	- TOTAL OUT	11.7 lbs.

5.2.7 Fluidizing Mechanics

There are numerous types of reactors for contacting activated carbon with gases. From the standpoint of smaller equipment, of the resulting decreased investment, of high heat transfer rates, and good solids flow characteristics, multistage fluidized bed reactors were chosen as the type of gas/solid contactor. There are many important parameters to be considered in design of the fluid bed reactor. The gas/solid residence time requirements have been discussed in previous sections as related to the process chemistry.

Westvaco has developed considerable technology in fluid bed design and operation. In addition to the basic process development of fluid bed design data, which had been developed prior to the present contract, some aspects relating to the fluidizing mechanics have been studied under the present contract. Those points are discussed below.

Carbon Fluidization Requirements -

As presently conceived, SO_2 sorption and sulfur generation steps will be run in fluidized beds of activated carbon. These fluidized beds operate at linear gas velocities between the minimum fluidizing (U_{Mf}) and entrainment velocities (U_t). Kunii and Levelspiel[9] present equations for calculating these bed characteristics, i.e.

Minimum fluidizing velocity, U_{Mf}

$$U_{Mf} = \frac{\mu}{d_p\rho_g}\left[(33.7)^2 + 4.08(10^{-2})\,\frac{d_p\rho_g(\rho_s - \rho_g)g}{\mu^2}\right]^{1/2} - 33.7 \qquad (65)$$

Terminal velocity, U_t

$$U_t = \left[\frac{3.1\ g\ (\rho_s - \rho_g)d_p}{\rho_g}\right]^{1/2} \qquad 500 < Re_p < 200{,}000 \qquad (66)$$

where $Re_p = \frac{D_p U_t \mu_g}{\mu}$

The calculation of minimum fluidizing velocity and entrainment velocity for Westvaco granular carbon, which has an average particle size of 0.1 cm and a particle density of 1.0 g/cm^3, is shown in Table 60.

Table 60. CALCULATED VALUES FOR MINIMUM FLUIDIZING VELOCITY AND ENTRAINMENT VELOCITY FOR WESTVACO GRANULAR ACTIVATED CARBON

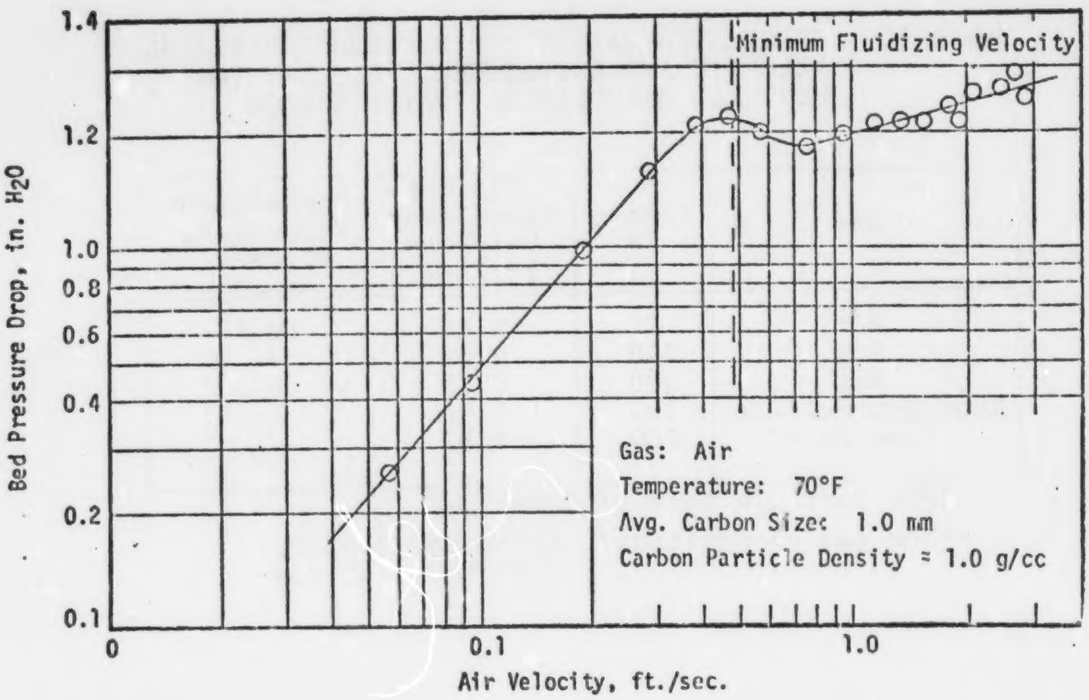
Gas	Temp., °F	Minimum Fluidizing Velocity, ft./sec.	Entrainment Velocity*, ft./sec.
Air	70	0.84	10.7
Air	200	0.87	--
Air	300	0.75	--
Hydrogen Sulfide	300	0.86	--
Flue Gas**	200	0.82	--

*For particle size of 0.042 cm.

**For gas composition: 76.6% N_2, 3.4% O_2, 6.0% H_2O, 14% CO_2

As can be seen from the table, there is very little difference between the calculated values for air over the range 70-300°F. In addition there is little difference between the minimum fluidizing velocities calculated for air, H_2S and flue gas. Thus fluidization characteristics with air at 70°F can be used to closely approximate fluidization parameters for SO_2 sorption and sulfur generation. Actual experimental measurement of the minimum fluidizing velocity with Westvaco granular carbon is shown in Figure 74. The measured value, taken as the maximum in the curve as suggested by Levenspiel[9] is approximately 0.5 ft./sec. or about 40% below the calculated value. This is slightly outside the range of ±34% in which Levenspiel[9] says the values normally fall. The difference is probably due to the deviation of the irregular carbon particles from a true spherical shape.

Figure 74. Experimental determination of minimum fluidizing velocity for Westvaco granular carbon



Also shown in Table 60 is the calculated entrainment velocity of 10.7 ft./sec. for a 0.42 mm particle which is the smallest particle of significant percentage in the carbon sample. Thus, for the Westvaco granular carbon used in SO_2 removal, the range of operating velocities is the 0.5 ft./sec. (experimental value) minimum fluidizing velocity and the approximately 10.7 ft./sec. entrainment velocity. In the SO_2 sorber, it is desirable to run as high a velocity as practical in order to keep the adsorber cross-section as small as possible for treating the large volumes of flue gas. Since some smaller particles will be generated by the bed action, a value of about 8 times the minimum fluidizing velocity, or about 4 ft./sec., is used for the sorber. Since the sulfur generator will be much smaller than the sorber, a value of 4 - 6 times the minimum fluidizing velocity (~2.5 - 3.0 ft./sec.) should be sufficient to maintain good contact and minimize elutriation.

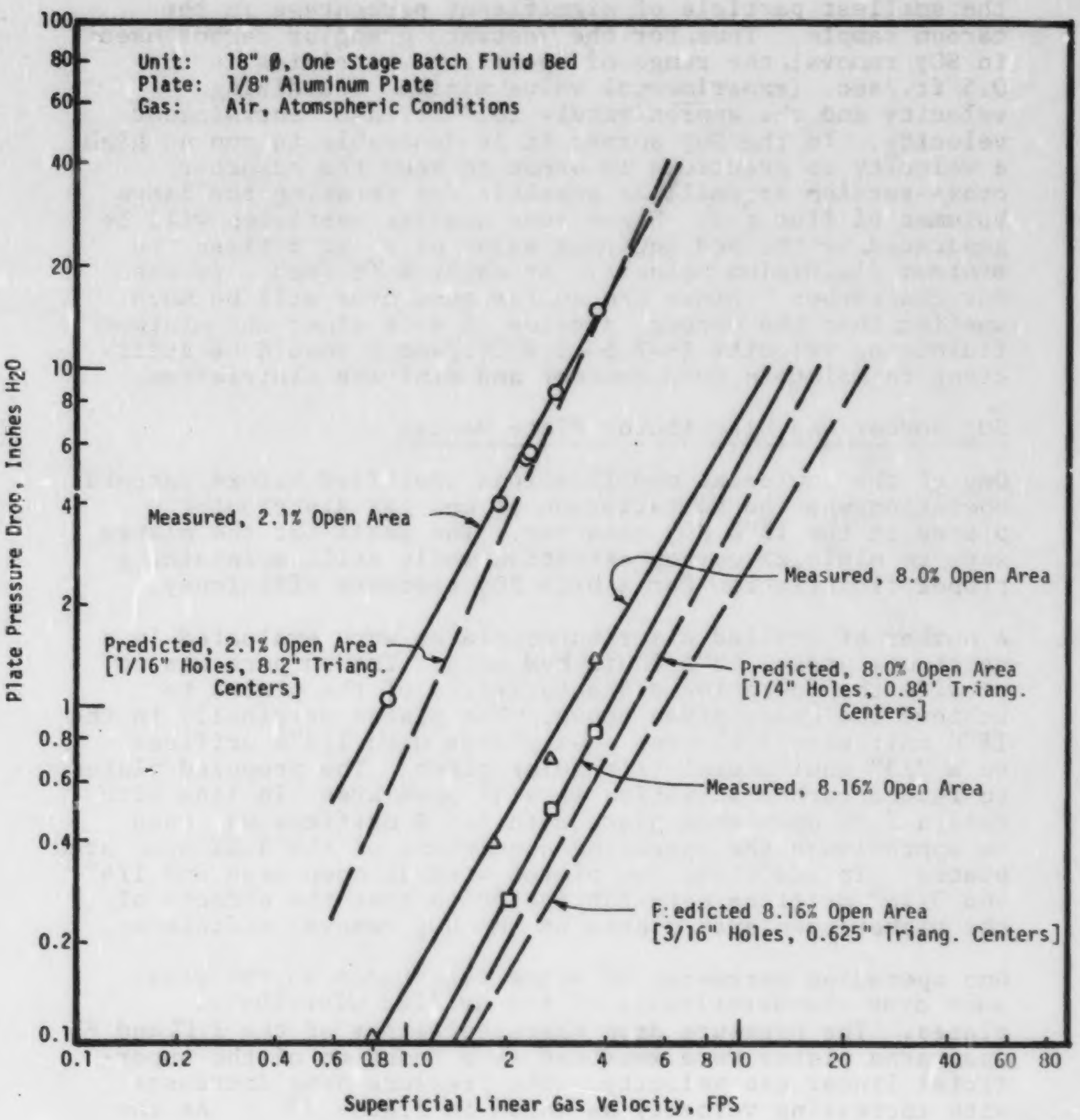
SO_2 Sorber Gas Distributor Plate Design -

One of the equipment modifications specified before integral operation was the installation of new gas distributor plates in the 18"Ø SO_2 adsorber. The goals for the plates were to minimize carbon attrition while still maintaining proper fluidization for a high SO_2 recovery efficiency.

A number of drilled distributor plates were evaluated in a batch, one stage, 18"Ø fluid bed unit. The purpose was to provide the operating characteristics of the plates to achieve the goals given above. The plates originally in the 18"Ø unit were 3.2% open area plates with 1/8"Ø orifices on a 2/3" equilateral triangular pitch. The proposed plates to reduce carbon attrition were 8% open area. In line with this, a 2.1% open area plate with 1/8"Ø orifices was used to approximate the operating conditions of the 3.2% open area plates. In addition, two plates with 8% open area and 1/4" and 3/16" orifices were fabricated to test the effects of the higher open area plates on the SO_2 removal efficiency.

One operating parameter of prime importance is the pressure drop characteristics of the drilled distributor plates. The pressure drop characteristics of the 2.1% and 8% open area plates were measured as a function of the superficial linear gas velocity. The pressure drop increases with increasing velocity as shown in Figure 75. As the open area increases the pressure drop decreases and as the orifice diameter decreases for a particular open area the pressure drop also decreases. The experimental data compares favorably with data taken from the literature. In terms of what can be expected in the 18"Ø SO_2 sorber, the pressure drop across the 3.2% open area plate is about 3" H_2O at

Figure 75. Pressure drop characteristics of distributor plates to be used in an 18" diameter SO_2 sorber



*Predicted from Smith and V. Winkle, AIChE 30:305-312(1957).

3 ft./sec. and with an 8% open area plate at 3 ft./sec. a pressure drop near 0.6" H_2O would be realized or a total pressure drop reduction across the plates of a factor or 5 or more.

The SO_2 sorption characteristics of the plates were determined by loading the bed with 35 lbs. virgin carbon, then at time zero the simulated flue gas (2,000 ppm SO_2, 200 ppm NO. 2 to 2.4% H_2O, balance air) was introduced into the fluid bed at 3 ft./sec. The total sulfur analysis of the carbon was then followed as a function of time. The run was stopped when the acid loading was above 0.22 lb. acid/lb. C. The results of the runs are given in Table 61. The SO_2 removal efficiency was 0.24, 0.22, and 0.15 for the 1/8", 3/16", and 1/4" hole diameter plates, respectively. An unanticipated problem occurred, however, with what is called carbon weepage during fluidization. This phenomena is carbon flow through the distributor plate, which in a continuous unit would mean possible short-circuiting of the carbon which could result in an inefficiency of the SO_2 sorber. The phenomena was only observed, at least to an appreciable extent, for the high open area plates (8%), with larger orifices. Nevertheless, on a qualitative basis it is felt that the SO_2 sorption efficiency is comparable in light of this carbon removal phenomena occurring continuously as a function of time.

Since the carbon weepage appeared important in the gas distributor design for the 18"Ø unit, the above plates and a number of other ones were evaluated for carbon weepage. The carbon weepage rate was investigated as a function of the open area, orifice diameter, superficial linear gas velocity, and carbon bed loading. The six plates which were evaluated are given in Table 62. The plates varied from 2.1% to 8.3% open area with 3/32"Ø to 1/4"Ø orifices.

The final carbon weepage rate data was subjected to a multiple regression analysis. The data was found to correlate well as given by Equation (67):

$$\Lambda = 8.4(10^{-11})\, e^{23.2\, d_o}\, e^{1.95\, A_o} \left(\frac{1}{v}\right)^{1.3} e^{0.12\, L} \qquad (67)$$

where Λ = carbon weepage rate, lb. C/hr.-ft.^{2}
d_o = orifice diameter, in.
A_o = gas distributor open area, %
v = superficial linear gas velocity, ft./sec.
L = carbon bed loading, lbs. C

Table 61. OPERATING CHARACTERISTICS DISTRIBUTOR PLATES TO BE USED IN AN 18" DIAMETER SO_2 SORBER

Run No.	PLATE CHARACTERISTICS							COLUMN CONDITIONS														SO_2 Removal Efficiency	****Carbon Weepage Rate	
	Overall Dia., in.	Thick. in.	Triang. Pitch in.	Hole Dia. in.	No. of Holes	Open Area %	Hole Velocity ft./sec.	Gas Flow, CFM @ 70°F	Super-ficial Gas Veloc. FPS	Gas Concentration SO_2 PPM	Gas Concentration NO PPM	Gas Concentration H_2O Vol. %	Gas Concentration Air	Carbon Type	Carbon Loaded lbs.	Run Time min.	Carbon End on Plate, lbs.	C in* Cyclone lbs.	C in** Plenum lbs.	Final Acid Load #Acid/#C			#/hr.	#/hr.-ft.^{2}
SA-42	18	1/8	0.84	1/8	440	2.1*****	142	278	3.0	2,000	200	2.0	Bal.	Virgin	35	240	30.5	2.2	***	0.235		0.24	---	---
SA-43	18	1/8	0.82	1/4	415	8.0	37	278	3.0	2,000	200	2.2	Bal.	Virgin	35	240	10.5	0.6	23.9	0.253		0.15	6.0	3.4
SA-44	18	1/8	0.625	3/16	750	8.2	36	271	2.9	2,000	200	2.4	Bal.	Virgin	35	180	10.3	0.7	24.0	0.244		0.22	8.0	4.5

*Cyclone dust given on total weight basis; was not analyzed for moisture and acid content.

**By difference since no analysis was made of carbon in plenum.

***Was not measured but discrepancy in material balance is believed due to start-up problems in which carbon may have bypassed cyclone.

****Taken as constant over time period of run.

*****Used to approximate 3.2% open area plate.

Table 62. **GAS DISTRIBUTOR PLATE CHARACTERISTICS EVALUATED FOR CARBON WEEPAGE DURING FLUIDIZATION**

Plate Diameter, inches	Orifice Diameter, inches	Triangular Pitch, inches	Plate Open Area, %
18	1/8	0.840	2.1
18	1/8	0.667	3.2
18	5/32	0.667	5.4
18	3/32	0.310	8.3
18	3/16	0.820	8.2
18	1/4	0.625	8.0

The correlation coefficient (R) for the equation was 0.95, which indicates a good fit of the model to the experimental data. Although larger orifice diameters up to 1/4"Ø were considered, the operating difficulties during start-up and shutdown make the 3/16"Ø and 1/4"Ø orifices unsuitable for the present pilot plant equipment. Therefore for the present plates, the orifice diameter was taken to be 1/8".

The carbon weepage rate for the present plates in the 18"Ø unit (L = 30 lbs., A_o = 3.2%, d_o = 1.8", and v = 3 ft./sec.) was predicted to be 6.7(10^{-6}) lbs. C/hr.-ft.^{2} or for the 18"Ø unit, 1.1(10^{-5}) lbs. C/hr., which is effectively zero. For the proposed 8% open area plates (1 = 30 lbs., A_o = 8%, d_o = 1/8", and v = 3 ft./sec.) the predicted carbon weepage rate is 0.14 lb. C/hr. This weepage rate is acceptable in the upper stages of the 18"Ø unit (about 0.5% of the total carbon flow rate through the unit), but is felt to be less desirable for the bottom stage in extended integral runs. This would correspond to 65 lbs. C which would be collected in the inlet gas plenum for the 18"Ø unit over a 20 day operation.

To minimize this carbon handling a 6.15% open area plate with 1/8"Ø orifices was considered and the predicted carbon weepage rate was 0.004 lb. C/hr. or about 2 lbs. C over a 20 day period. This is an acceptable quantity of carbon but is at the expense of a slightly higher carbon attrition rate, since the carbon attrition is a direct function of the per cent open area of the plate.

All of the experimental data led to the design of four distributor plates in the upper stages of 8% open area with 1/8"Ø orifices on a 0.42" equilateral triangular pitch. Two of the top uppermost stages are of aluminum and the other two are of 316 stainless steel. The distributor plate for the bottom stage was specified to be 6.15% open area with 1/8"Ø orifices on a 0.48" equilateral triangular pitch. The specifications for these distributor plates are given in Table 63.

Table 63. GAS DISTRIBUTOR PLATES SPECIFICATIONS DESIGNED FOR MINIMIZING CARBON ATTRITION IN THE 18"Ø SO_2 SORBER

Plate Diameter, inches	Orifice Diameter, inches	Triangular Pitch, inches	Plate Open Area, %
18	1/8	0.42	8.0
18	1/8	0.48	6.15

SECTION 6
1,000 MW UTILITY BOILER FLUE GAS CLEAN-UP

6.1 INTRODUCTION

The Westvaco Process has been developed over the past eight years, the last three under joint support from EPA. The process is designed to adsorb SO_2 out of flue gas streams with activated carbon and to produce elemental sulfur as a by-product. Pilot tests of the complete process treating 20,000 cfh of flue gas from an oil fired boiler have recently been completed under this EPA contract, and results are contained in this report.

With the Westvaco Process, sulfur dioxide is removed from waste gases with activated carbon acting as a catalyst and adsorbent in the reaction:

$$SO_2 + 1/2\ O_2 + H_2O \xrightarrow[\text{Carbon}]{\text{Activated}} H_2SO_4\ \text{(Sorbed)} \qquad [150\text{-}300°F] \qquad (5)$$

The sorbed acid is then converted to elemental sulfur by reaction with H_2S, with the carbon again acting as a catalyst and adsorbent:

$$H_2SO_4 + 3\ H_2S \xrightarrow[\text{Carbon}]{\text{Activated}} 4\ S\ \text{(Sorbed)} + 4\ H_2O \qquad [200\text{-}300°F] \qquad (6)$$

The sorbed elemental sulfur is then thermally stripped from the activated carbon at 800-1000°F and condensed as product. In utility applications where H_2S is unavailable for conversion of sorbed acid to sulfur, hydrogen is added to the gases during the thermal stripping step to produce the necessary amount of H_2S by the reaction:

$$H_2 + S\ \text{(Sorbed)} \xrightarrow[\text{Carbon}]{\text{Activated}} H_2S \qquad [800\text{-}1200°F] \qquad (68)$$

A schematic of the process is shown in Dwg. 2563 (Figure 76).

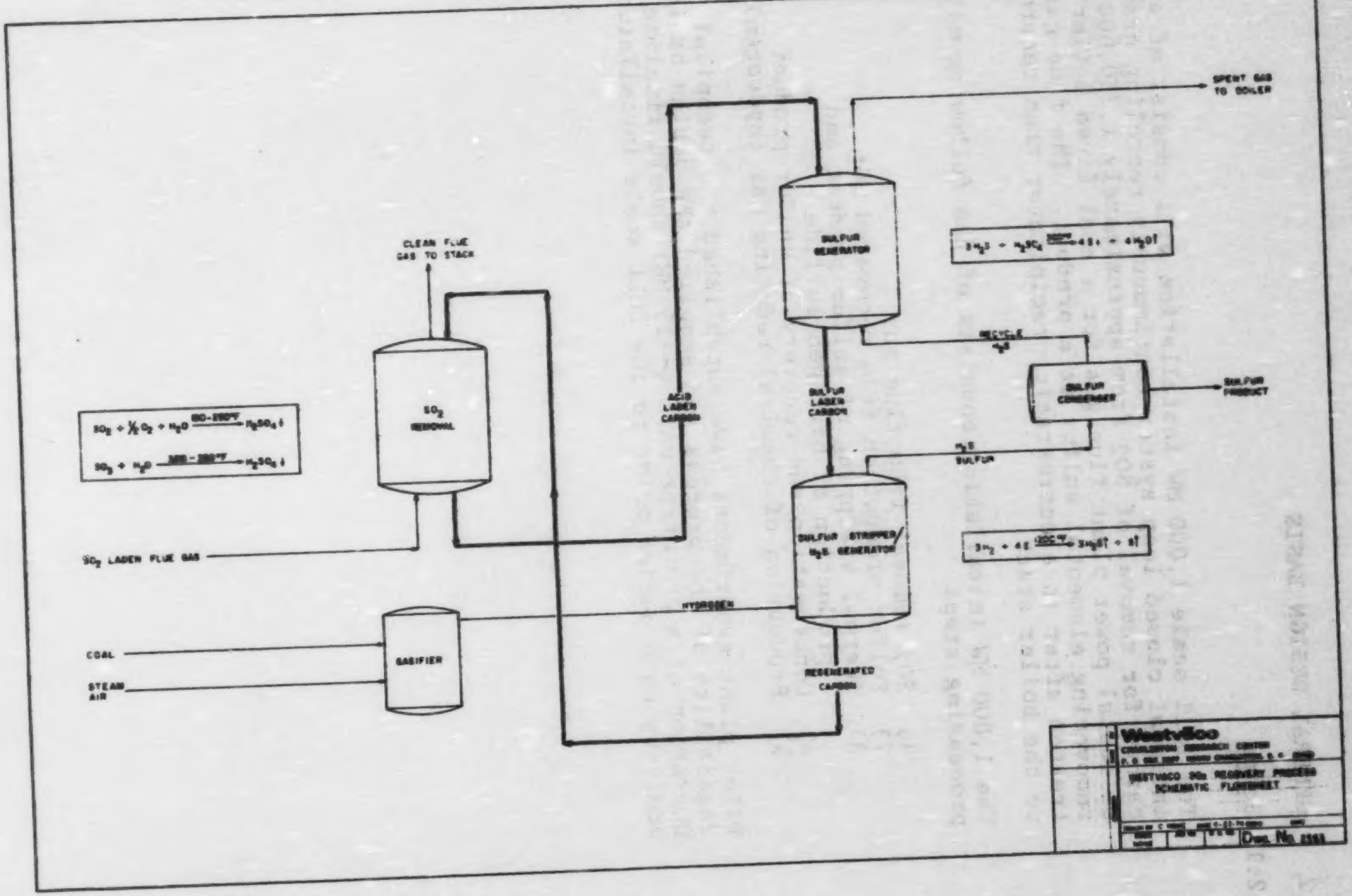

CLEAN FLUE GAS TO STACK
SO2 REMOVAL
SO2 LADEN FLUE GAS
COAL
STEAM AIR
GASIFIER
HYDROGEN
ACID LADEN CARBON
SULFUR LADEN CARBON
SULFUR GENERATOR
SULFUR STRIPPER/ H2S GENERATOR
REGENERATED CARBON
RECYCLE H2S
H2S SULFUR
SULFUR CONDENSER
SULFUR PRODUCT
SPENT GAS TO BOILER
SO2 + ½O2 + H2O → H2SO4
SO3 + H2O → H2SO4
3H2S + H2SO4 → 4S + 4H2O↑
3H2 + 4S → 3H2S↑ + S↑
Westvaco
CHARLESTON RESEARCH CENTER
WESTVACO SO2 RECOVERY PROCESS SCHEMATIC FLOWSHEET
Dwg. No.

Figure 76. Westvaco SO2 Recovery Process schematic flowsheet

6.2 GENERAL DESIGN BASIS

6.2.1 Scope

The full scale 1,000 MW installation will consist of an integral closed loop system continuously recycling granular carbon for removal of SO_2 from approximately 1,750,000 cfm of actual power plant flue gas for a coal fired boiler and recovering elemental sulfur as a product. The flue gas is treated after an electrostatic precipitator then returned to the boiler stack.

The 1,000 MW installation consists of the following major processing steps:

1) SO_2 removal from flue gas
2) Sulfur production from recovered SO_2
3) Thermal stripping of sulfur product and production of hydrogen sulfide
4) Condensation and recovery of sulfur product
5) Production of chemical reducing gas (hydrogen).

Pilot plant experiments have established the technical feasibility of the process and supplied the design basis. Operation of a prototype unit (~15 MW) should finalize scale-up data needed prior to the full scale installation.

6.2.2 Boiler Operating Characteristics

Coal Composition -

Component, Ash:	15.2% Dry Wt. %
Sulfur:	3.5 Dry Wt. %
Hydrogen:	5.0 Dry Wt. %
Carbon:	67.2 Dry Wt. %
Nitrogen:	1.6 Dry Wt. %
Oxygen:	7.5 Dry Wt. %
H_2O in Coal:	4.8 lbs./100 lbs. Wet
Excess Air:	20%
Carbon Burned in Coal:	100%
Heating Value in Coal:	Wet - 11,980 BTU/lb. Dry - 12,580 BTU/lb.
Sulfur to SO_2:	98%
Sulfur to SO_3:	2%
SO_2 Removal:	90%
Flue Gas Temp. Out of Air Preheater:	300°F
Minimum Gas Temp. to Stack after Treatment:	200°F
Gas Velocities in Ducts:	60 ft./sec.
Plant Size:	1,000 MW
Heat Rate:	9,000 BTU/KWHR.
Flue Gas Quantity:	293,000 moles/hr.
Flue Gas Molecular Wt.:	29.54
Flue Gas Weight:	8,655,000 lbs./hr.

Flue Gas Composition -

Component, SO_2:	0.00261 mole fraction
SO_3:	0.00005 mole fraction
CO_2:	0.13657 mole fraction
Nitrogen:	0.74087 mole fraction
Oxygen:	0.03276 mole fraction
Water:	0.08714 mole fraction
Fly Ash:	77,900 lbs./hr.
Water in Combustion Air (60% RH @ 80°F):	0.0212 mols/mol dry air
Coal Consumption Rate (Wet):	751,252 lbs./hr.

Gas Ducts 300°F or Higher To Be Insulated

6.2.3 Product

Type: Elemental Sulfur
Purity: 99.8% or Better - Bright Yellow
Form: Liquid at 250°F

6.2.4 Process Conditions

SO_2 Sorber -

Reaction: $SO_2 + \frac{1}{2} O_2 + H_2O \rightarrow H_2SO_4$

Heat of Reaction: Exothermic = -117,000 BTU/mole SO_2

Contact Mode: Stagewise Gas/Solid Fluidized Bed

Fluidizing Gas Velocity: 4 FPS (At Base Load of 1,000 MW)

Fluidized Bed Temperature: 150-300°F

SO_2 Overall Recovery Efficiency: 90%

SO_2 Rate (At Base Load), from Coal = 48,943 # SO_2/hr.
from Recycle = 7,782 # SO_2/hr.
TOTAL = 56,725 # SO_2/hr.

Acid Loading on Carbon: 0.22 lb. H_2SO_4/lb. C

Number of Stages: 5

Space Velocity: 2,350 $hr.^{-1}$

Carbon Bed Depth/Stage: 11 inches

Carbon Rate: 43 Tons Carbon/Hr. (At Base Load)

SO_2 Concentration, Inlet (Coal) = 2,610 PPM
(Recycle) = 415
TOTAL = 3,025 PPM
Outlet: 245 PPM

Boiler Feed H_2O Spray Rate: 183 GPM

Sulfur Production -

Reaction: $H_2SO_4 + 3 H_2S \rightarrow 4 S + 4 H_2O$

Heat of Reaction: Exothermic = -41,107 BTU/mole H_2SO_4

Contact Mode: Stagewise Gas/Solid Fluidized Bed

Fluidizing Gas Velocity: 3 FPS (At Base Load)

Fluidized Bed Temperature: 200-325°F

Inlet H_2S Concentration: 2 Vol. %

Conversions, H_2S Utilization: 99.9% of Inlet H_2S
SO_2 Recycle: 15% of Sorbed H_2SO_4
Sulfur Formation: 70% of Sorbed H_2SO_4

Number of Stages: 11

Space Velocity: 460 hr.$^{-1}$

Carbon Bed Depth/Stage: 17 Inches

Carbon Rate: 43 Tons/Hr. (At Base Load)

Outlet H_2S Concentration: 270 PPM

Sulfur Stripping/H_2S Generation -

Reaction: a) $H_2 + S \rightarrow H_2S$
b) $H_2SO_4 + 3\ H_2S \rightarrow 4\ S + 4\ H_2O$

Heat of Reaction: a) Exothermic = -8,667 BTU/mole H_2SO_4
b) Exothermic = -41,107 BTU/mole H_2SO_4

Contact Mode: Stagewise Gas/Solid Fluidized Bed

Fluidizing Gas Velocity: 3 FPS (At Base Load)

Fluidized Bed Temp.: a) Carbon Preheater = 710°F
b) H_2S Gen./S Strip. = 1000-1200°F

Inlet H_2 Concentration: 19.5%

Inlet H_2 Requirement: 3.3 moles H_2/mole SO_2 recovered

Carbon Residence Time: 21 minutes

Design Rates (At Base Load): a) S Stripping = 796 moles S/hr.
b) H_2S Formation = 1,910 moles H_2S/hr.

Number of Stages: a) Carbon Preheater = 1
b) H_2S Formation = 2
c) Sulfur Stripping = 4

Space Velocity: 1600 hr.$^{-1}$

Sulfur Recovery -

Type: Shell and Tube Condenser

Duty: 796 moles S/hr.

Temperature: a) Inlet Gas = 1040°F
b) Outlet Gas = 250°F
c) S Liquid Prod. = 250°F

Efficiency: 99.9% of Inlet Sulfur

Carbon Cooler -

Contact Mode: Gas/Solid Fluidized Bed

Fluidizing Gas Velocity: 3 FPS

Fluidized Bed Temperature: a) Inlet C = 1040°F
b) Outlet C = 300°F
c) Outlet Gas = 300°F

Gas Type: a) Recycled Inert Gas
b) 5% Inert Gas Make-up/Cycle
c) 5% Boiler Feed H_2O Make-up/Cycle

Number of Stages: 1

Gasifier -

Type: Bituminous Coal Feed

Product Gas: 28 cf $(H_2 + CO)$/lb. Coal
65 cf Total Gas/lb. Coal

6.2.5 Activated Carbon Characteristics

Type:	Coal Based
Size:	8x30 M [Nominal; 1.5 MM (Avg. Particle Size)]
Density:	40 - 43 lbs./ft.^{3}
SO_2 Number:	75 (Minimum)
Attrition No.:	30 (Maximum)

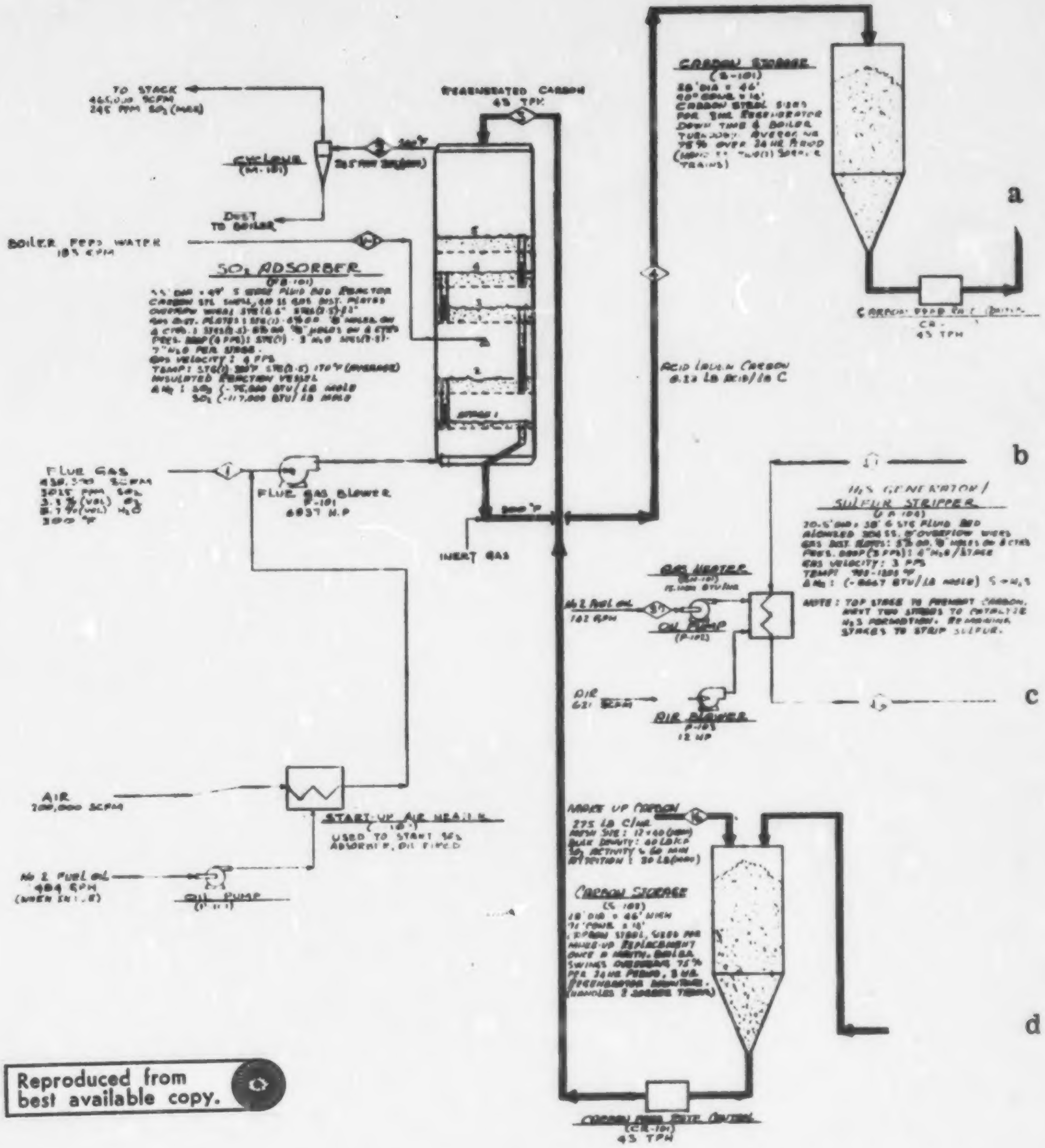
6.3 CONCEPTUAL DESIGN

The conceptual design flowsheet for the process is shown in Figure 77 (Dwg. 2572) and described by the process description below.

6.3.1 Process Description

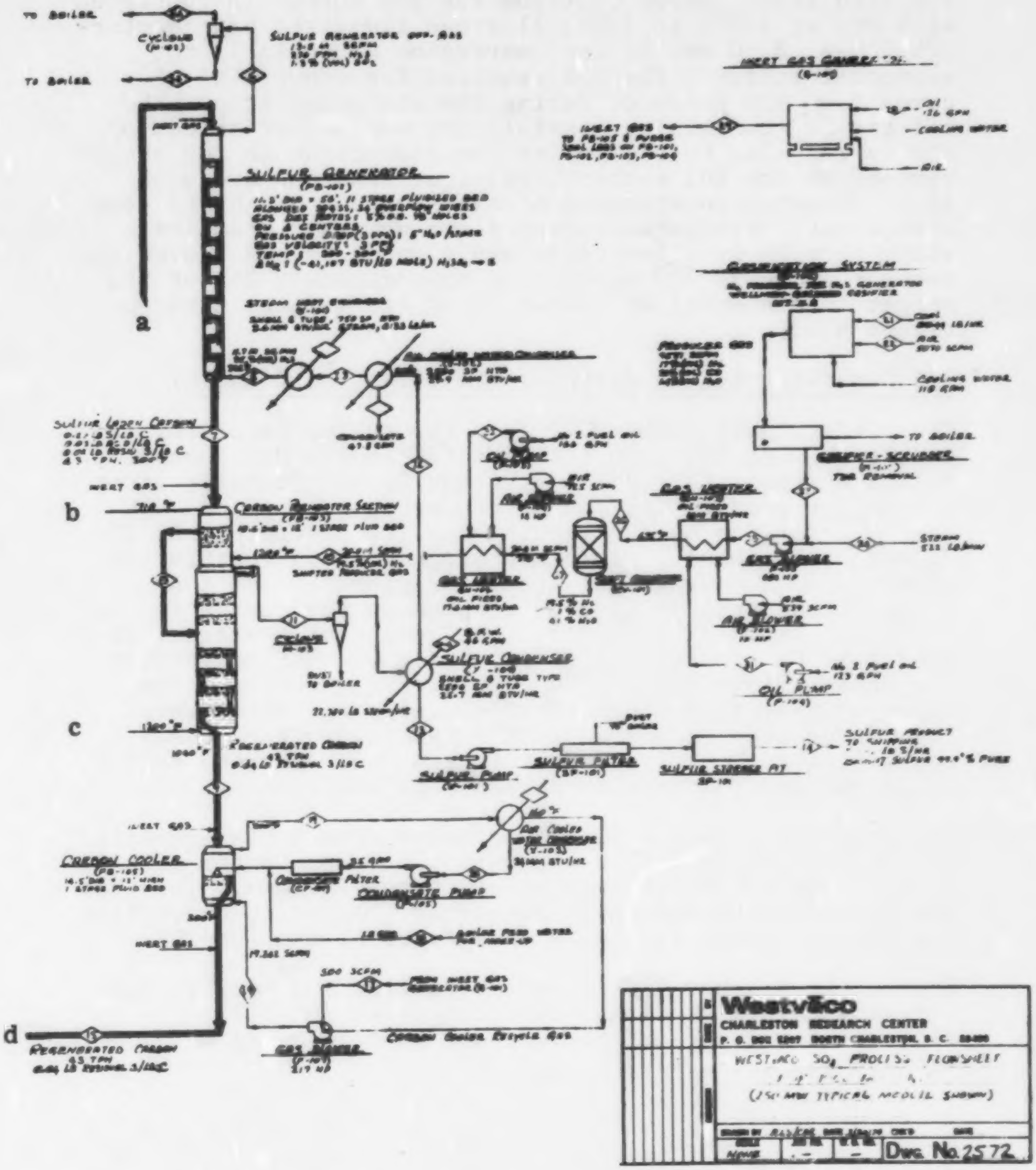
SO_2 Sorber - Boiler Flue Gas (FB-101-A, B, C and D) -

The boiler flue gas <1> is desulfurized by counter-current contact with regenerated carbon <3> in stagewise fluid bed reactors (FB-101-A, B, C and D). The total flue gas volume of 105 million SCFH is split among four 55' diameter mild steel sorbers containing 5 stages of fluidized carbon for SO_x removal. The bottom stage removes SO_3 at 300°F to prevent acid condensation. The gas temperature is then lowered to 170°F for more efficient SO_2 removal by direct evaporation of water sprayed into the second fluid bed stage. The remaining 4 fluid bed stages, containing 13.5 inches of activated carbon each, lower the SO_2 concentration to 245 ppm at the outlet <2>. Reaction heat liberated during SO_2 removal reheats the gas temperature to 200°F. The fluidized carbon flows down the column by gravity through overflow weirs and downcomers becoming progressively loaded with sulfuric acid and leaves the column <4> at 300°F containing 22% of its weight in adsorbed acid.


TO STACK
465,000 SCFM
245 PPM SO_2 (MAX)
CYCLONE
(M-101)
DUST TO BOILER
REGENERATED CARBON
43 TPH
BOILER FEED WATER
183 GPM
SO_2 ADSORBER
(FB-101)
55' DIA × 49' 5 STAGE FLUID BED REACTOR
CARBON STL SHELL
GAS VELOCITY: 4 FPS
INSULATED REACTION VESSEL
STAGE 1
FLUE GAS
438,370 SCFM
3015 PPM SO_2
3.3 % (VOL) O_2
8.7 % (VOL) H_2O
300 °F
FLUE GAS BLOWER
P-101
6837 H.P
INERT GAS
AIR
200,000 SCFM
START-UP AIR HEATER
USED TO START SO_2 ADSORBER, OIL FIRED
No 2 FUEL OIL
484 GPM
OIL PUMP
CARBON STORAGE
(S-101)
58' DIA × 46'
CARBON STEEL
ACID LADEN CARBON
0.12 LB ACID/LB C
CARBON FEED RATE CONTROL
CR-
43 TPH
a
b
H_2S GENERATOR/
SULFUR STRIPPER
20.5' DIA × 38' 6 STG FLUID BED
GAS VELOCITY: 3 FPS
NOTE: TOP STAGE TO PREHEAT CARBON, NEXT TWO STAGES TO CATALYZE H_2S FORMATION. REMAINING STAGES TO STRIP SULFUR.
GAS HEATER
No 2 FUEL OIL
102 GPH
OIL PUMP
(P-102)
AIR
621 SCFM
AIR BLOWER
P-103
12 HP
c
MAKE UP CARBON
275 LB C/HR
MESH SIZE: 12 × 40
BULK DENSITY: 40 LB/CF
ATTRITION: 30 LB(MAX)
CARBON STORAGE
(S-102)
18' DIA × 46'
CARBON STEEL
d
CARBON FEED RATE CONTROL
(CR-101)
43 TPH

Reproduced from best available copy.

Figure 77. Westvaco SO_2 Process flowsheet for 1,000 MW unit (250 MW typical module shown)


TO BOILER
CYCLONE
TO BOILER
SULFUR GENERATOR OFF-GAS
SULFUR GENERATOR
(FB-101)
a
STEAM HEAT EXCHANGER
CONDENSATE
SULFUR LADEN CARBON
INERT GAS
b
CARBON REGENERATOR SECTION
SHIFTED PRODUCER GAS
CYCLONE
DUST TO BOILER
SULFUR CONDENSER
SHELL & TUBE TYPE
c
REGENERATED CARBON
1000°F
INERT GAS
CARBON COOLER
(FB-105)
CONDENSATE FILTER
CONDENSATE PUMP
AIR COOLED WATER CONDENSER
INERT GAS
d
REGENERATED CARBON
GAS BLOWER
CARBON COOLER RECYCLE GAS
500 SCFM
SULFUR PUMP
SULFUR FILTER
SULFUR STORAGE PIT
SULFUR PRODUCT TO SHIPPING
OIL PUMP
No. 2 FUEL OIL
AIR BLOWER
GAS HEATER
SHIFT CONVERTER
GAS HEATER
GAS BLOWER
AIR BLOWER
OIL PUMP
No. 2 FUEL OIL
123 GPM
STEAM
GASIFIER - SCRUBBER
TAR REMOVAL
TO BOILER
GASIFICATION SYSTEM
PRODUCER GAS
COAL
AIR
COOLING WATER
118 GPM
INERT GAS GENERATOR
INERT GAS
OIL
126 GPM
COOLING WATER
AIR
Westvaco
CHARLESTON RESEARCH CENTER
WESTVACO SO₂ PROCESS FLOWSHEET
(250 MW TYPICAL MODULE SHOWN)
NONE
Dwg. No. 2572

A blower (F-101) is included to overcome the gas pressure drop in each adsorber. A start-up heater (A-101) is included for pre-heating the sorber.

Sulfur Generator (FB-102-A, B, C and D) -

The acid laden carbon ⟨4⟩ from the SO_2 sorber is contacted with H_2S at 300°F in four, 11 stage fluidized bed reactors (FB-201-A, B, C and D) for conversion of the acid to elemental sulfur. The H_2S required for conversion ⟨5⟩ comes from H_2S produced during the stripping step. The off-gas ⟨6⟩ containing possibly SO_2 evolved or traces of H_2S is recycled to the boiler for conversion to SO_2 easily removed in the SO_2 sorber. The four reactors are each 11.3' diameter constructed of Alonized 304 stainless steel throughout. Activated carbon flows downward from stage to stage through overflow weirs and downcomers and leaves the reactor at 300°F ⟨7⟩ containing approximately 24% of its weight in elemental and about 3% of its weight in unconverted acid.

H_2S Generator/Sulfur Stripper (FB-103-A, B, C and D) -

The sulfur laden carbon ⟨7⟩ from the sulfur generator is contacted with hydrogen rich gas ⟨10⟩ in the H_2S generator/sulfur stripper (FB-103-A, B, C and D) to thermally strip the sulfur product ⟨14⟩ and to produce a part of the H_2S feed ⟨12⟩ for the sulfur generator. The reactor is 20'6" diameter, contains 7 fluidized stages and is constructed of Alonized 304 stainless steel throughout. The top stage of the reactor is used to preheat the carbon to 710°F and is 18'7" diameter. The remaining 6 stages, at 1000-1050°F, are for sulfur stripping and H_2S conversion. The carbon flows down through the vessel from stage to stage by gravity through overflow weirs and downcomers. The regenerated carbon at 1050°F ⟨9⟩ leaves the vessel containing 4.1% of its weight in residual adsorbed sulfur which remains constant throughout the whole loop.

The hydrogen rich gas ⟨10⟩ is produced from a coal gasifier [G-102] in series with a water-gas shift converter (CV-101-A, B, C and D) for conversion of CO to hydrogen. Tars are removed prior to the shift converter. After CO conversion the gas is heated to 1040°F in a fired heater [GH-102].

The sulfur product ⟨13⟩ is separated from the recycle H_2S stream ⟨12⟩ in a shell and tube condenser (SC-101), filtered for traces of carbon, and sent to a sulfur storage pit (SP-101).

Carbon Cooler (FB-105-A, B, C and D) -

After regeneration the carbon is cooled to 300°F by direct evaporation of water sprayed into the fluidized bed cooler (FB-105-A, B, C and D). Recycle inert gas is used as the fluidized gas. The 14.5' diameter cooler contains one stage and is of Alonized 304 stainless steel construction. The H_2O is condensed from the recycle gas and both are reused.

Carbon Handling and Storage -

Activated carbon is recirculated through the process loop at a rate of 172 tons per hour. Storage for 6 hours of carbon recirculation is provided for both the acid laden and regeneration loop to accommodate variation in waste gas rates. The storage vessels (S-101 and -102) are coned bottom tanks 28'Ø x 60' tall of mild steel construction. The total carbon inventory is 2,000 tons and make-up carbon is added at a rate of 275 lbs./hr. Horizontal and vertical conveying are accomplished by belt conveyors and bucket elevators, respectively. These are not detailed on the flow sheet but are described in the equipment lists in Appendix K.

6.4 HEAT AND MATERIAL BALANCES

The heat and material balances were made for the overall process just described. The overall sulfur balance is shown in Table 64. The overall sulfur balance reiterates the 90% sulfur recovery from the flue gas taken as a basis for this particular evaluation.

Table 64. OVERALL SULFUR BALANCE FOR
1,000 MW POWER PLANT

SULFUR IN		SULFUR OUT	
Stream	lbs. S/hr.	Stream	lbs. S/hr.
Flue Gas	24,940	Flue Gas	2,494
Gasifier Gas	896	Elemental S Product	23,342
TOTAL IN = 25,836		TOTAL OUT = 25,836	

The overall energy balance is given in Table 65. About 60% of the total heat input originates with the flue gas, indicating the relative energy requirement of the regeneration system.

Table 65. OVERALL ENERGY BALANCE FOR
1,000 MW POWER PLANT

ENERGY INPUT			ENERGY OUTPUT		
Stream	MM BTU/Hr.	%	Stream	MM BTU/Hr.	%
Flue Gas	554	48.7	Flue Gas	284	25.0
Spray H_2O	57	2.4	Spray H_2O Vap.	367	32.2
ΔH_{rxn} - SO_x Removal	96	8.4	Reducing Gas	13	1.1
ΔH_{soln} - H_2O-H_2SO_4	17	1.5	ΔH_{soln} H_2O-H_2SO_4	17	1.5
ΔH_{rxn} - S Gen.	24	2.1	H_2O Vap. - H_2O-H_2SO_4	16	1.4
ΔH_{rxn} - H_2S Gen.	31	2.7	Sulfur Vap.	4	0.4
Sulfur Cond.	4	0.4	ΔH_{rxn} - H_2S Generator	6	0.5
Gasifier Gas	1	0.1	Sulfur Product	2	0.2
Steam for Shift Run	12	1.1	Sulfur Condenser	103	9.1
Reducing Gas Preheat	126	11.1	Carbon Cooler - H_2O Vap.	83	7.3
Reducing Reheat	60	5.3	Carbon Cooler - H_2O Rec.	96	8.4
Reducing H_2O Cond.	98	8.6	H_2O Condenser	112	9.8
Reducing Reheat	14	1.2	H_2O Condensed from R.G.	3	0.3
Carbon Cooler H_2O Cond.	74	6.5	Heat Losses - Carbon Storage	32	2.8
TOTAL IN = 1,138 MM BTU/Hr.			TOTAL OUT = 1,138 MM BTU/Hr.		

The detailed heat content and stream compositions are given in Tables 66 - 75.

Table 66. STREAM CONDITIONS

	STREAM 1		STREAM 2		STREAM 3		STREAM 4	
	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2		844		78				
H_2S								
H_2SO_4							78,944	
Elemental S								
O_2		9,612		9,208				
H_2O		25,520		43,388			14,276	
N_2		217,112		217,112				
CO_2		40,140		40,140				
H_2								
SO_3		16						
CO								
CH_4								
C_2H_6								
Residual S			10		13,664		13,654	
Carbon			258		341,556		341,298	
TOTAL		293,284	268	309,926	355,220		448,222	
M SCFM	1,753		1,850		---		---	
Temp., °F	330		200		77		300	
Press., in. H_2O	+40		+10		---		---	
Heat, MM BTU/Hr.	554		284		0		26	

Table 67. STREAM CONDITIONS

	STREAM U-1		STREAM 5		STREAM 6		STREAM 7	
	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2						102		
H_2S				1,850		2.1		
H_2SO_4							11,916	
Elemental S							77,769	
O_2								
H_2O	364,960			680		3,688	2,264	
N_2				3,036		3,036		
CO_2				1,872		1,872		
H_2								
SO_3								
CO				132		132		
CH_4				160		160		
C_2H_6				28		28		
Residual S							13,654	
Carbon							341,287	
TOTAL	364,960			7,846		9,037	446,890	
M SCFM	---		11.7		13.5		---	
Temp., °F	150		325		325		300	
Press., in. H_2O	---		59		4		---	
Heat, MM BTU/Hr.	27		15.9		12.5		26.4	

Table 68. STREAM CONDITIONS

	STREAM 8		STREAM 9		STREAM 10		STREAM I-1	
	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2								182
H_2S						28		28
H_2SO_4								
Elemental S	75,824							
O_2								
H_2O						5,496		5,616
N_2						3,036		3,036
CO_2						1,872		1,872
H_2						2,608		2,608
SO_3								
CO						132		132
CH_4						160		160
C_2H_6						28		28
Residual S	13,654		13,654					
Carbon	341,287		341,281					
TOTAL	430,765		354,934			13,360		13,664
M SCFM	---		---		79.9		81.8	
Temp., °F	710		1040		1300		710	
Press., in. H_2O	---		---		109		105	
Heat, MM BTU/Hr.	76.4		112		139		70.0	

Table 69. STREAM CONDITIONS

	STREAM I-2		STREAM 11		STREAM 12		STREAM 13	
	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2		182		1,850		1,850		1,850
H_2S		28						
H_2SO_4			23,344					
Elemental S								
O_2		5,616		5,984		5,984		680
H_2O		3,036		3,036		3,036		3,036
N_2		1,872		1,872		1,872		1,872
CO_2		2,605						
H_2								
SO_3		132		132		132		132
CO		160		160		160		160
CH_4		28		28		28		28
C_2H_6								
Residual S			0.2					
Carbon			6					
TOTAL		13,664		13,150		13,150		7,846
M SCFM	81.8		78.7		78.7		46.9	
Temp., °F	1200		1040		250		110	
Press., in. H_2O	91		67		63		61	
Heat, MM BTU/Hr.	130		119		18.4		2.1	

Table 70. STREAM CONDITIONS

	STREAM 1-3		STREAM 14		STREAM 15		STREAM 16	
	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2								
H_2S								
H_2SO_4								
Elemental S	23,344		23,344					
O_2								
H_2O								
N_2								
CO_2								
H_2								
SO_3								
CO								
CH_4								
C_2H_6								
Residual S					13,653		3	
Carbon	1				341,281		275	
TOTAL	25,457		25,456		354,934		278	
M SCFM	---		---		---		---	
Temp., °F	250		250		300		77	
Press., in. H_2O	---		---		---		---	
Heat, MM BTU/Hr.	1.6		1.6		19.4		0	

Table 71. STREAM CONDITIONS

	STREAM 17		STREAM 18		STREAM I-4		STREAM 19	
	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2								
H_2S								
H_2SO_4								
Elemental S								
O_2								
H_2O		12	3,676			3,769		7,855
N_2		258				7,280		7,280
CO_2		64				1,812		1,812
H_2								
SO_3								
CO								
CH_4								
C_2H_6								
Residual S								
Carbon								
TOTAL		334	3,676			12,860		16,947
M SCFM	2.0		---		77.0		101	
Temp., °F	77		150		150		300	
Press., in. H_2O	2		---		9		4	
Heat, MM BTU/Hr.	0		0.3		7.1		29.5	

Table 72. STREAM CONDITIONS

	STREAM 20		STREAM 21		STREAM 22		STREAM 23	
	lbs./hr.	moles/hr.			lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2								
H_2S								28
H_2SO_4								
Elemental S								
O_2						824		
H_2O	69,864					3,100		90
N_2								3,036
CO_2								326
H_2								1,062
SO_3								
CO								1,678
CH_4								160
C_2H_6								28
Residual S								
Carbon								
TOTAL	69,864					3,924		6,408
M SCFM	---				23.5		38.3	
Temp., °F	160				---		100	
Press., in. H_2O	---				---		2	
Heat, MM BTU/Hr.	5.6				---		1.0	
Tons Coal/Hour			17.7					

Table 73. STREAM CONDITIONS

	STREAM 24		STREAM 25		STREAM 26		STREAM 26	
	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2								
H_2S				28		28		28
H_2SO_4								
Elemental S								
O_2								
H_2O	125,136			7,042		7,042		5,496
N_2				3,036		3,036		3,036
CO_2				326		326		1,872
H_2				1,062		1,062		2,608
SO_3								
CO				1,678		1,678		132
CH_4				160		160		160
C_2H_6				28		28		128
Residual S								
Carbon								
TOTAL	125,136			13,360		13,360		13,360
M SCFM	41.6		79.9		79.9		79.9	
Temp., °F	280		200		675		710	
Press., in. H_2O	---		166		155		150	
Heat, MM BTU/Hr.	11.6		12.0		63.2		68.6	

Table 74. STREAM CONDITIONS

	STREAM 28		STREAM 29		STREAM 30		STREAM 31	
			lbs./hr.	moles/hr.	lbs./hr.	moles/hr.		
SO_2								
H_2S								
H_2SO_4								
Elemental S								
O_2								
H_2O				24				
N_2				516				
CO_2				128				
H_2								
SO_3								
CO								
CH_4								
C_2H_6								
Residual S								
Carbon								
TOTAL				668				
M SCFM			4.0					
Temp., °F			77					
Press., in. H_2O			2					
Heat, MM BTU/Hr.			0					
# No.2 Fuel Oil/Hr.	1.027				4,146		3,592	

Table 75. STREAM CONDITIONS

	STREAM 32		STREAM		STREAM		STREAM	
			lbs./hr.	moles/hr.	lbs./hr.	moles/hr.	lbs./hr.	moles/hr.
SO_2								
H_2S								
H_2SO_4								
Elemental S								
O_2								
H_2O								
N_2								
CO_2								
H_2								
SO_3								
CO								
CH_4								
C_2H_6								
Residual S								
Carbon								
TOTAL								
M SCFM								
Temp., °F								
Press., in. H_2O								
Heat, MM BTU/Hr.								
# No. 2 Fuel Oil/Hr.	4,847							

6.5 COSTS OF 1,000 MW CONCEPTUAL DESIGN INSTALLATION

6.5.1 Cost Summary

Based on the conceptual design flowsheet, heat and material balances, the costs estimated for installation of the Westvaco Process on a 1,000 MW boiler are summarized below:

Table 76. COST SUMMARY

Capital Cost		Operating Cost	
$ Million	$/KW	$ Million/Yr.	Mil/KWH
35	35	14.6	2.0

Details of the estimate are discussed in the following sections and back-up information is contained in Appendix K.

6.5.2 Capital Costs

The conceptual design flowsheet was used to estimate the cost of installing a Westvaco Process in a 1,000 MW power boiler. The summary is given in Table 77.

6.5.3 Equipment Costs

Purchased equipment cost estimates were based on actual vendor quotes when available. When quotes were not available, standard engineering estimating procedures were used. This led to a basic purchased equipment cost. The total direct installation cost was then obtained by factors given by Miller[10]. The detailed estimate is given in Appendix K.

Table 77. CAPITAL COST SUMMARY

Basic Equipment Costs	$ 7,278,100
Equipment Installation Costs	7,350,900
Cost of Additional Battery Limit Items	5,611,800
TOTAL DIRECT COST - BATTERY LIMIT	20,240,800
Auxiliary Costs (Storage, Auxil., Serv.)	1,619,200
TOTAL BATTERY LIMIT + AUXILIARIES	21,860,000
Catalyst Costs (Carbon + Shift Catalyst)	1,703,200
TOTAL DIRECT COST	$23,563,200

Engineering & Supervision Cost	$ 3,298,800
Construction Cost	2,356,300
Contractor's Fee	942,600
Contingency	4,712,600
TOTAL INDIRECT COST	$11,310,300

TOTAL INSTALLED COST = $\boxed{\$34,873,500}$

6.5.4 Indirect Costs

The indirect costs are made up of engineering, construction, contractor's fee, and an estimating contingency. Factors for obtaining these costs are given by Peters and Timmerhaus[11]. The factor used for contingency was more than twice that suggested by Peters and Timmerhaus.

6.6 OPERATING COSTS OF 1,000 MW CONCEPTUAL DESIGN INSTALLATION

The annual operating costs for the Westvaco Process at a 1,000 MW installation is about $14.6 million/year or 2.08 mills/KWH. The operating utilities estimates were based on operation of the installation on an 80% yearly basis. These operating basis and capital cost change factors were the same as those used by M. W. Kellogg in an earlier comparison of the process to other SO_2 removal processes.

The annual operating cost is given in Table 78. The total direct costs were $7.3 million/yr. if no sulfur credit is taken and $5.5 million/yr. if minimal credit were taken. The indirect cost was about $1 million/yr. and the fixed cost was $6.3 million/yr. This led to gross operating costs of $14.6 million/yr. or 2.08 mills/KWH if no sulfur credit is taken. The net operating cost is $12.8 million/yr. or 1.83 mills/KWH if minimal sulfur credit is taken.

Table 78. ANNUAL OPERATING COSTS

PLANT SIZE (MW): 1,000
FIXED CAPITAL INVESTMENT (FCI): $34,873,500
STREAM TIME (HRS./YR.): 7,000

		$/Year $40/Lb. Carbon
DIRECT COST		
1.	Operating Labor (4 Men/Shift @ $5.50/Hr.)	154,000
2.	Supervision - 15% of Item 1	23,100
3.	Maintenance, Labor & Materials - 4% of FCI	1,394,900
4.	Plant Supplies - 15% of Item 3	209,200
5.	Utilities	
	a. Cooling Water - 1,430 GPM @ $0.10/M Gal.	60,100
	b. Boiler Feed Water - 924 GPM @ $.15/M Gal.	58,200
	c. Electric Power - 26,600 KW @ $6.75 Mills/KWH	1,256,900
	d. No. 2 Fuel Oil - 2,260 GPH @ $0.12/Gal.	1,898,400
	e. Coal - 17.6 TPH @ $12/Ton	1,478,400
6.	Chemicals & Raw Materials	
	a. Activated Carbon - 275 lbs./hr. @ $0.40/lb.	770,000
7.	SUBTOTAL Direct Cost (Excl. Credits)	7,303,200
8.	Credits	
	a. Sulfur - 305 TPD @ $20/Short Ton	-1,779,200
9.	TOTAL DIRECT COST	5,524,000
INDIRECT COST		
10.	Payroll Overhead - 20% of (1+2)	35,400
11.	Plant Overhead - 50% of (1+2+3+4)	890,600
12.	TOTAL INDIRECT COST	926,000
FIXED COST		
13.	Capital Charges - 18.22% of FCI (Includes Depreciation Interim Replacements, Insurance, Taxes and Cost of Capital)	6,354,000
TOTAL OPERATING COST		
14.	Net Production Cost - Items (9+12+13)	12,804,000
UNIT PRODUCTION COST		
15.	Gross - Items (7+12+13)	14,583,200
	a. Mills/KWH	2.08
	b. $/Ton Sulfur Not Emitted	163.9
16.	Net - Items (9+12+13)	
	a. Mills/KWH	1.83
	b. $/Ton Sulfur Not Emitted	143.9

SECTION 7
15 MW DESIGN AND COST

7.1 INTRODUCTION

The technical feasibility of the Westvaco Process has been demonstrated in a 20,000 cfh integral pilot unit. A detailed assessment of the process indicated economic viability and competitiveness with other systems proposed for sulfur gas control. The following section outlines the program and cost to test the process on a large scale in an actual utility. The test program is designed to generate operating data for more detailed process assessment and to demonstrate reliability and compatability with utility operation.

7.2 SCOPE OF THE PROTOTYPE PROGRAM

The technical feasibility of the Westvaco Process has been demonstrated in integral pilot plant tests. In order to obtain engineering information for a detailed economic assessment and for process scale-up, a prototype program is proposed for testing at the 15 MW (30,000 cfm) level. The scope of the program is to assess the process performance and to obtain engineering data on the major questions related to:

1. Compatability with the boiler interface
   a. turndown, upsets and outage in boiler
   b. reliability
   c. fuel feed variations
   d. safety

2. Control of process chemistry
   a. response to upsets and variations
   b. long term stability

3. Performance of activated carbon
   a. mechanical
   b. chemical

4. Performance of large scale fluid bed vessels
   a. solid distribution
   b. gas distribution
   c. ease of operation.

In attaining these objectives the scope of this program includes:

1. Definition of boiler operating characteristics
2. Preparation of detailed prototype test program
3. Preparation of prototype design specifications
4. Detailed engineering design and bid evaluation
5. Construction
6. Start-up
7. Operation
8. Data evaluation and process technical and economic assessment.

As an adjunct to the prototype program the scope of work will also include, as necessary, additional testing in the current pilot and other equipment to refine the prototype design as seems necessary.

7.3 DESCRIPTION OF PROTOTYPE PLANT AND OPERATION

7.3.1 General

The prototype plant will consist of an integral closed loop system continuously recycling granular carbon for removal of SO_2 from approximately 30,000 cfm of actual power plant flue gas from a coal fired boiler and recovering elemental sulfur as a product.

The prototype size is equivalent to about 15 MW of the boiler capacity with design capabilities to handle 10 - 20 MW. The flue gas will be withdrawn between an electrostatic precipitator and the boiler stack. The desulfurized flue gas from the prototype plant will be returned to the stack.

The prototype plant consists of the following major processing steps:

1. SO_2 removal from flue gas.
2. Sulfur production from recovered SO_2
3. Thermal stripping of sulfur product and production of hydrogen sulfide
4. Condensation and recovery of sulfur product
5. Production of chemical reducing gas (hydrogen).

Pilot plant experiments have established the technical feasibility of the process and supplied the data base for the prototype design basis. In the general design basis that follows, specifications are given to accommodate the range of conditions anticipated in the test program and demonstration run.

7.3.2 General Design Basis

Boiler Characteristics -

Size Equivalent: 15 MW (30,000 scfm equivalent)

Type of Fuel: Coal

Sulfur Content: 1 - 4%

Load Variation: 10 - 20 MW

Flue Gas: 20,000 - 40,000 scfm; 800 - 3100 ppm SO_2

Process Conditions -

SO_2 Sorber -

Reaction: $SO_2 + \frac{1}{2} O_2 + H_2O \rightarrow H_2SO_4$

Heat Release: 117,000 BTU/mol SO_2

Contact Mode: Gas/Solid Fluidized Bed, Stagewise

Fluidizing Gas Velocity: 2 - 4 ft./sec.

Space Velocity: 2,350 $hr.^{-1}$ (Design Based on Experimental Rate Model)

Fluidized Bed Temperature: 150 - 300°F

Carbon Feed Rate: 4.4 - 8.8 M lbs./hr.

SO_2 Rate: 250 - 1,000 lbs./hr.

Sulfur Production -

Reaction: $3 H_2S + H_2SO_4 \rightarrow 4 S + 4 H_2O$

Heat Release: 41,107 BTU/mol S

Contact Mode: Fluidized Bed, Stagewise

Inlet Gas: 50,800 scfh with 22% H_2S

Gas Velocity: 3 ft./sec.

Space Velocity: 475 $hr.^{-1}$ (Design Based on Experimental Rate Model)

Temperature: 250 - 325°F

Carbon Feed Rate: 6,600 lbs./hr. (Average)

Carbon Residence Time: 40 minutes

Sulfur Formation Rate: 1,328 lbs./hr.

Sulfur Stripping/H_2S Formation -

Reaction: a) $H_2 + S \rightarrow H_2S$
b) $3\ H_2S + H_2SO_4 \rightarrow 4\ S + 4\ H_2O$ (Overall)

Heat Release: a) 8,667 BTU/mol S
b) 41,107 BTU/mol S

Contact Mode: Fluidized Bed, Stagewise

Inlet Gas: 92,600 scfh with 19.4% H_2

Gas Velocity: 3 ft./sec. @ 1000°F

Space Velocity: 1600 $hr.^{-1}$ for C preheat and S stripping
3800 $hr.^{-1}$ for H_2S formation

Temperature: 715°F (Preheat); 1000°F (Stripping)

Carbon Feed Rate: 6600 lbs./hr. (Average)

Carbon Residence Time: 21 minutes [3.5 min. (Preheat) + 17.5 minutes (Stripping)]

Design Rates: 419 lbs./hr. (S Stripping)
187 cfm (H_2S Formation)

Sulfur Recovery -

Type: Condenser, Shell and Tube

Duty: 500 lbs. S/hr.; 2 MM BTU/hr.

Temperature: 940°F, Inlet Gas
260°F, Outlet Gas
260°F, Liquid Product

Efficiency: 99.5% of Inlet Sulfur

Gasifier -

Type: Coal Feed with Steam/Air Blast

Feed: 716 lbs./hr. Bituminous Coal (Maximum)
716 lbs./hr. Anthracite Coal (Maximum)

Product Gas: 28 cf H_2 + CO/lb. Coal

Activated Carbon Characteristics -

Size: 8x30 Mesh (Nominal; 1.5 MM Avg. Particle Size)

Density: 40 - 43 $lbs./ft.^3$

SO_2 Number: 75 (Minimum)

Attrition No.: 30 (Maximum)

Instrumentation -

Adequate instrumentation is included, based on pilot plant experience, to control and monitor temperature, pressure, gas and carbon flow, and gas composition. Additional instrumentation is also included in the design to assess the various methods of overall process control under the varying modes of utility boiler operation.

In addition to the major equipment items, auxiliary equipment such as blowers, heat exchangers, conveyors, dust collectors, etc. are included in the final design to accommodate the range of operating conditions defined for the major equipment items. Details of these items are listed in Appendix L.

7.3.3 Process Description - Prototype Plant (Dwg. 2573, Fig. 78)

Flue gas from the precipitator at 300°F passes first through the flue gas blowers (F-101) where the pressure is boosted and then into the SO_2 adsorber (FB-101). The adsorber is 16 feet in diameter and contains five fluidized stages of activated carbon. Sulfur trioxide is removed from the hot gases in the bottom stage of the adsorber. Water sprays above the second stage cool the gas to 170°F prior to completion of the 90% sulfur oxide removal in this and the remaining three stages. Conversion of sulfur dioxide to sulfuric acid during sorption by the activated carbon reheats the flue gas ⟨3⟩ to 200°F. A cyclone collector (M-101) removes entrained carbon dust from the flue gas prior to its return to the stack. The normal dust loading of the clean flue gas from the cyclone would be about .01 gr/scf with a maximum expected of .02 gr/scf. A baghouse is included to measure the efficiency of the cyclone and evaluate the total attrition rate. Recycled activated carbon ⟨3⟩ continuously passes through the adsorber by gravity at a rate of 6,605 lbs./hr. where it is loaded with 22.0 lbs. H_2SO_4/lb. carbon. The H_2SO_4 is produced by sorption and conversion of the SO_2 in the flue gas.

Sulfuric acid laden carbon from the adsorber ⟨4⟩ is fed to the sulfur generator (FB-102) by a bucket elevator (V-101) and feeder (V-201). In the sulfur generator (FB-102), a 3' diameter, 11 stage fluid bed, the sorbed sulfuric acid is converted to elemental sulfur by reaction with hydrogen sulfide ⟨8⟩ at 300°F. The heat of reaction is dissipated by interstage water sprays as necessary. The activated carbon becomes progressively loaded with elemental sulfur

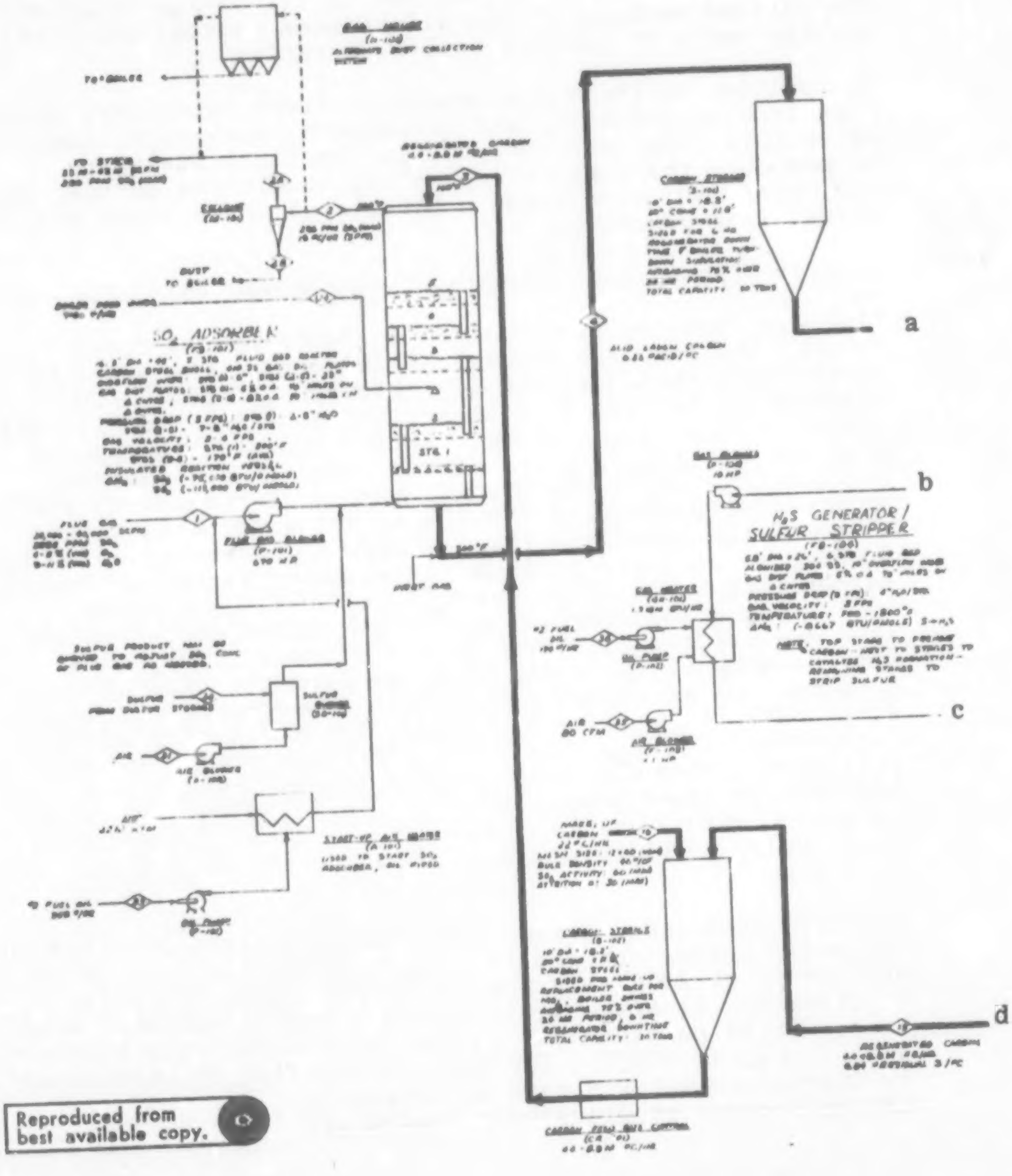

SO₂ ADSORBER
STG. 1
H₂S GENERATOR / SULFUR STRIPPER
a
b
c
d

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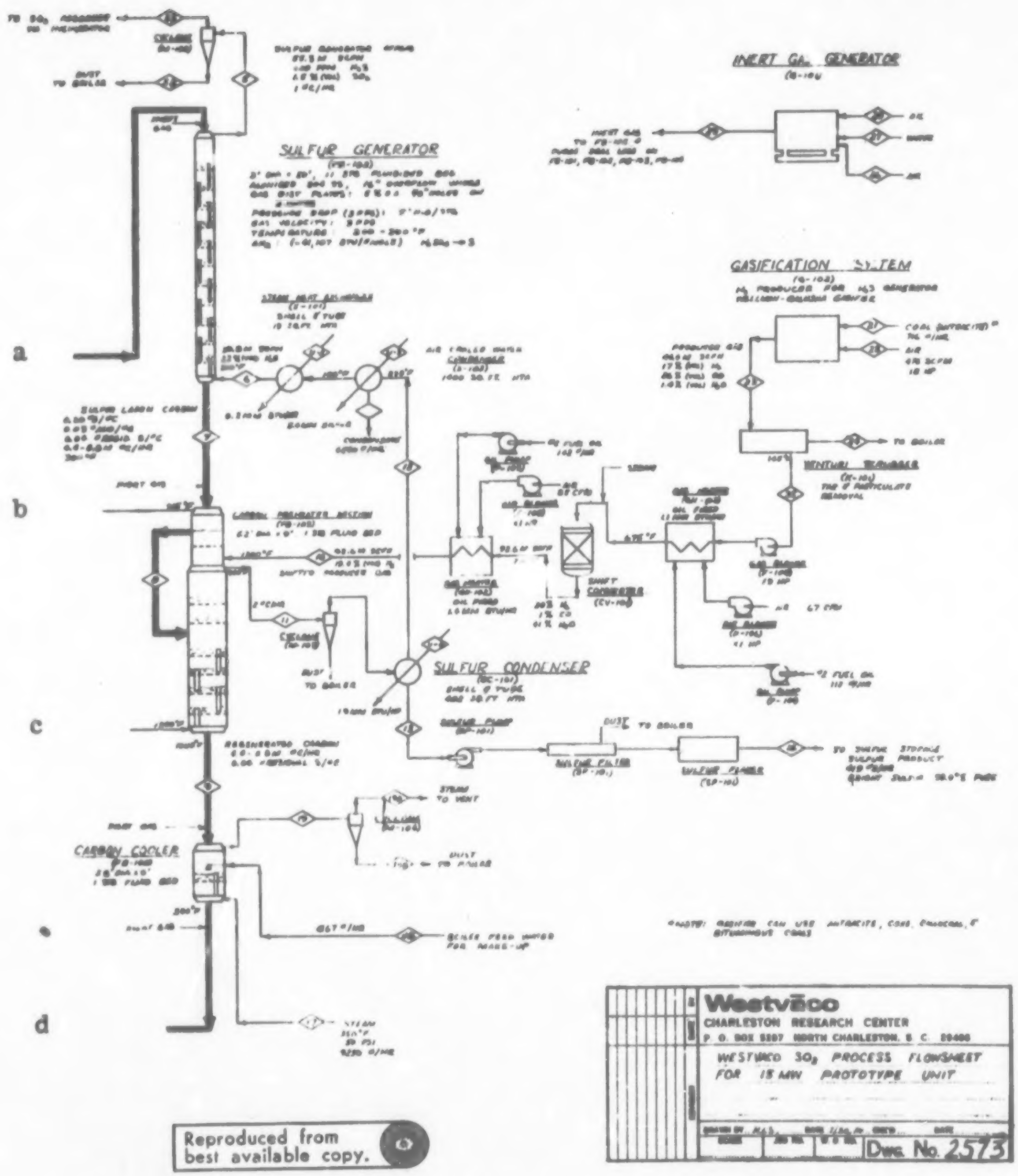
Figure 78. Westvaco SO_2 Process flowsheet for 15 MW prototype unit


SULFUR GENERATOR
(FB-102)
INERT GAS GENERATOR
(G-104)
GASIFICATION SYSTEM
(G-102)
SULFUR CONDENSER
(SC-101)
CARBON COOLER
VENTURI SCRUBBER
SULFUR FILTER
SULFUR PUMP
CYCLONE
TO BOILER
a
b
c
d
Westvaco
CHARLESTON RESEARCH CENTER
P. O. BOX 5207 NORTH CHARLESTON, S. C. 29406
WESTVACO SO2 PROCESS FLOWSHEET
FOR 15 MW PROTOTYPE UNIT
Dwg. No. 2573

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as it flows by gravity through the sulfur generator and exits with a loading of 20 lbs. S/100 lbs. C <7>. The additional sulfuric acid not converted to sulfur in this reactor is converted in the H_2S generator/sulfur stripper.

The elemental sulfur product is recovered by thermally stripping concurrently with H_2S formation in the H_2S generator/sulfur stripper (FB-104). The H_2S generator/sulfur stripper is a 70" diameter, 7 stage fluid bed with 1 stage for carbon preheat, 2 stages for H_2S formation, and 4 stages for stripping. The carbon is preheated with the reducing gas at 1300°F containing about 20 vol. % H_2. The carbon flows from the preheat stage at 715°F, bypassing two stages for H_2S formation, to four stages for sulfur removal at 940 - 1000°F. The off-gas from the carbon preheater is reheated to 1300°F and passed to the bottom of the H_2S generator/sulfur stripper where it contacts counter-currently the carbon to thermally strip the sulfur. The hydrogen and sulfur subsequently are converted to the H_2S necessary for sulfuric acid conversion in the sulfur generator. Final conversion of any remaining acid to sulfur also occurs in the sulfur stripper/H_2S generator. The gas leaves the H_2S generator/sulfur stripper at 940°F and passes to a shell and tube sulfur condenser to recover the elemental sulfur. The liquid sulfur at 270°F is filtered of any dust before being solidified by a sulfur flaker. The cooled gas at 270°F is effectively free of sulfur. The regeneration gas is supplied by a gas producer capable of gasifying anthracite, coke, charcoal, or bituminous coal. The gas from the gasifier passes through a shift converter before being used in the carbon preheater-H_2S generator/sulfur stripper.

Regenerated carbon <15> from the H_2S generator at 1000°F is cooled to 300°F in the carbon booler (E-501). Cooling is by evaporation of water sprayed over the single bed of fluidized carbon in the 70" diameter unit. Superheated steam used as the fluidizing gas passes through a cyclone and is exhausted.

The regenerated and cooled carbon <3> is then returned to the storage hopper for the adsorber. Make-up carbon is added to this hopper intermittently as needed.

7.3.4 Heat and Material Balances

Complete heat and material balances were performed for the prototype unit and part of the information is contained on the flowsheet. The complete stream compositions and heat contents are included in Appendix L.

7.3.5 Start-up and Initial Operation

The operating schedule for the prototype plant calls for a three month period of start-up, a three month test program and a six month demonstration run.

The start-up period will be used to work through the plant putting all units into operation, checking their operability over the specified temperature, flow and pressure ranges, and making any required adjustments, modifications or replacements. At the conclusion of the start-up period, the plant will be capable of accepting flue gas and circulating carbon through the adsorption and regeneration equipment.

The initial operating period will be devoted primarily to establishing the operating characteristics of the process. A material and heat balance will be obtained around the plant which will be checked against calculated values to determine if any significant deviations are occurring. The SO_2 removal capability on both a once-through basis and as a function of the number of cycles for a limited number of cycles will be determined. The process control characteristics, particularly stability and turndown capability, will be tested. These data will be analyzed as they are obtained. At the conclusion of the initial operating period, the data will be reviewed and any changes needed in the program for demonstration operation will be made.

7.3.6 Demonstration Operation

The demonstration operating period is intended to show the capability of the Westvaco Process to operate reliably under actual industrial conditions. The level of staffing of the plant will be reduced to that anticipated commercially. Boiler operating personnel will be used to the greatest extent possible. The primary responses being monitored during this period will be catalyst activity and attrition characteristics, process stability and control. Process operating information will be obtained for use in scale-up design.

The equipment will be inspected and photographed. The condition of all critical components will be noted.

7.3.7 Technical and Economic Review of Operation

After the initial and demonstration runs in the prototype plant, a technical and economic review will be made of the process. All pertinent information will be incorporated into a final report covering the technical data and presenting an economic evaluation of the process.

7.4 TECHNICAL APPROACH

7.4.1 General

The overall intent of the program is to assess the Westvaco Process on a 15 MW slipstream of a coal fired boiler. Prior to the engineering of the unit, Westvaco will prepare a detailed program for the equipment operation and process design specifications for the unit. These will be used by an applications-engineering firm to prepare the detailed design of the system and obtain bids for fabrication and erection. After the acceptance of bids, both Westvaco and the engineering company will monitor fabrication and erection. Prior to start-up, Westvaco will train technicians for operation during the test program and operators to be supplied by the utility who will operate the unit during the demonstration period. Data reduction, evaluation and process assessment will be performed jointly by Westvaco and the applications-engineering firm.

During the construction of the prototype unit, tests will be made to define fully the operating characteristics of the boiler as they would affect process operation.

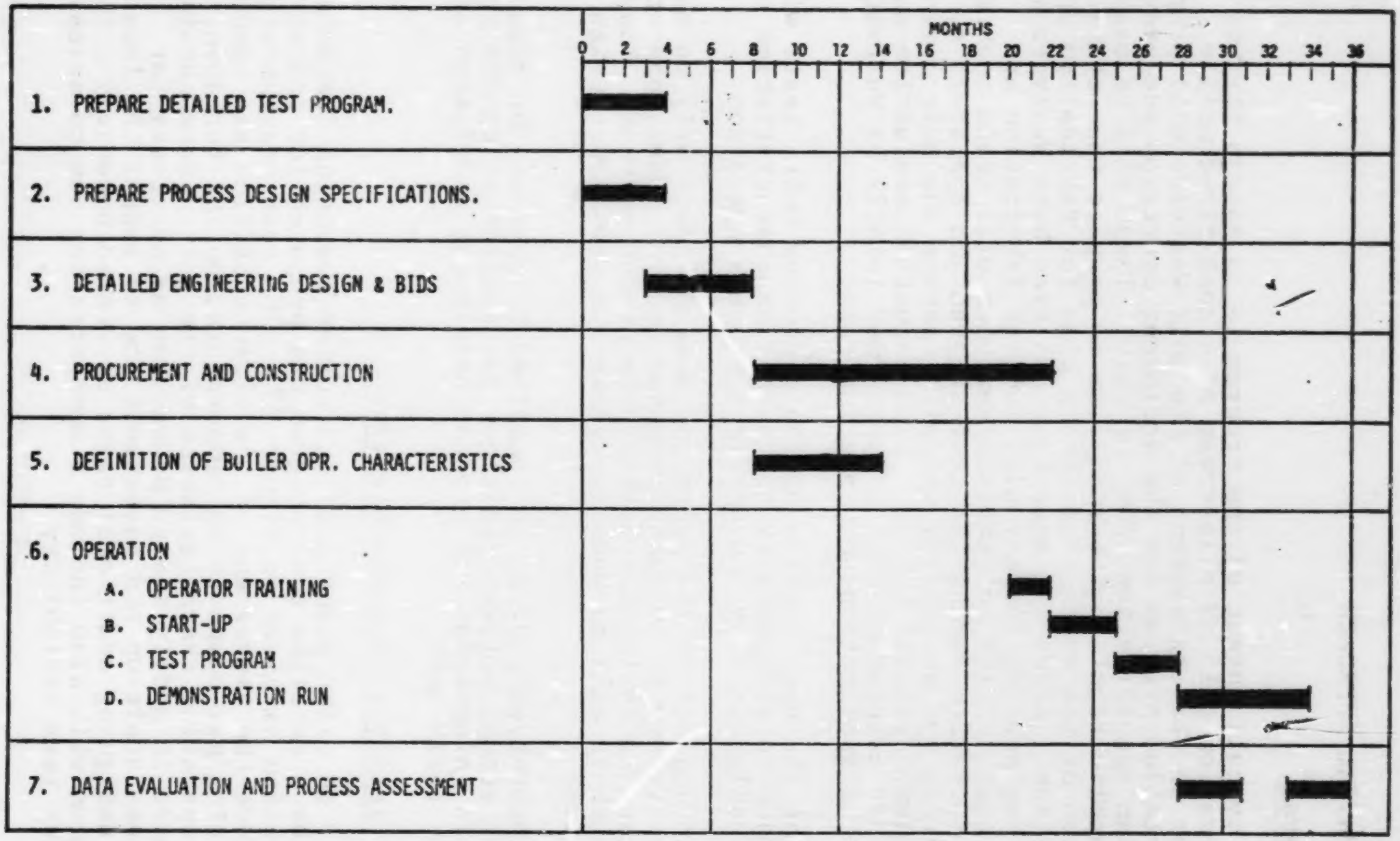
As an adjunct to the prototype design, tests will be made as necessary to evaluate proposed control modes, operating ranges and design features of the prototype unit. Input from these will be used to modify the prototype design as required.

The prototype program is conceived to operate the process under actual boiler conditions for sufficient cycles to obtain information for process assessment and design of a large scale unit.

7.4.2 Description of Program Elements

Based on pilot plant data and boiler operating characteristics a detailed test program was prepared for prototype operation as given in Figure 79. The test program will include the assessment of the effects of flue gas composition, reducing gas composition temperature, boiler turndown, etc. on the operating characteristics of the unit. Data obtained will be used to modify design procedures as necessary for process scale-up and assessment and to supply the input for designing additional tests as deemed necessary. The program will also include a demonstration run to assess longer term reliability.

Figure 79. Prototype program schedule



Based on the proposed test program and the pilot plant data available, detailed process design specifications for the prototype unit will be prepared by the process developer. This will include the general design basis, process description, heat and material balances, process equipment specifications, instrument list, proposed layout and utilities requirements. This will be assembled in report form for use by the applications-engineering firm to prepare a detailed design.

Using the process design specifications report from Westvaco, the applications-engineering company will prepare a detailed design of the prototype unit and secure bids for its fabrication and construction.

The engineering contractor will procure and construct the prototype unit.

During the construction phase an analytical program will be conducted to define the characteristics of the boiler operation. This will include: coal composition, flue gas composition and temperature and load variation. Tests will be conducted at intervals in order to establish trends.

During the construction phase operating manuals will be prepared and training programs conducted to familiarize development support personnel and selected plant operators with the operation of the recovery process.

The start-up will include sequential testing of the prototype equipment to achieve design operating characteristics. Modifications will be made as necessary. Operators will be given actual experience in equipment operation.

The test program will evaluate steady state and transient behavior of the system with variations in flue gas composition, reducing gas composition, temperature, boiler load, etc. An anticipated 100 - 125 cycles will be completed during the test program.

A six month demonstration run will be conducted to define the long term reliability of the process. Over the six month period 300 - 360 process cycles would be completed and there would be 1.25 - 1.5 complete inventory turn-overs.

Beginning with the test program there would be continuing analysis of data. This would be incorporated in a detailed assessment at the end of the test program which would be updated after the demonstration run.

7.5 COST OF PROTOTYPE PROGRAM

The summary of costs for the prototype program is shown below in Table 79:

Table 79. COST OF PROTOTYPE PROGRAM

1.	Installed Equipment		$2,411,000
2.	Design Engineering		240,000
3.	Manpower, R&D	$303,246	
	Operation	78,300	
	Maintenance	63,288	444,834
4.	Overhead		422,600
5.	Consultants		14,400
6.	Travel		14,400
7.	Raw Mat'l., Utilities & Supplies		321,760
	TOTAL COST		$3,868,994

The total prototype cost was estimated as follows:

Purchased equipment costs were estimated using general engineering methods and budget quotes from the equipment lists contained in Appendix L. The total installed equipment cost was derived from the purchased equipment cost based on the factors given by Miller[10]. The cost breakdown is shown in Appendix L.

Engineering costs were estimated from factors presented in Peters and Timmerhaus[11].

The required manhours for R&D, operators and maintenance were derived using the development schedule and assigning manhours based on experience in Westvaco's prior development work and plant experience. The manhour breakdown and cost breakdown are shown in Appendix L.

A provisional overhead on manpower costs was estimated at 95% of direct labor costs based on past experience.

Raw materials and utilities were determined from energy and material balances for the prototype unit and applied to the number of operating hours at rates shown in Appendix L.

SECTION 8
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SECTION 9

NOMENCLATURE

A - Constant

a - Constant

A_o - Gas Distributor Open Area, %

B - Constant

b - Constant

C - Gas Concentration, lb. moles/ft.^{3}

D - Reactor Diameter

d_o - Orifice Diameter

E - Activation Energy

F - Molar Flow Rate

g - Function

H_2S - Hydrogen Sulfide Gas Concentration

h - Carbon Bed Height

k - Rate Constant

k_o - Frequency Factor for Arrhenium Equation

L - Equilibrium Sulfur Loading Sorbed Carbon or Carbon Bed Loading

L_c - Amount of Sulfur Chemisorbed by Carbon

N - Moles

N_o - Initial Moles

P - Equilibrium Vapor Pressure of Sulfur

P_s - Saturation Vapor Pressure of Sulfur with Carbon

q - Gas Flow Rate or Differential Heat of Adsorption of Sulfur by Carbon

R - Gas Law Constant or Carbon Flor Rate

Re - Reynolds Number

r - Rate of Reaction
S - Sulfur Gas Concentration as S
T - Temperature
t - Time
U - Gas Velocity
V - Reactor Volume
v - Superficial Linear Gas Velocity, ft./sec.
X - Carbon Loading, weight of material/weight of carbon
$[\frac{M}{32}]_T$ - Average Number of Sulfur Atoms/Molecule

Greek Symbols

ρ - Density
μ - Viscosity
Λ - Carbon Weepage Rate

Subscripts

c - Carbon
g - Of Gas Phase
H - Hydrogen
H_2O - Water
H_2S - Hydrogen Sulfide
j - Stage Number j
$j+1$ - Stage Number j+1
Mf - Minimum Fluidizing
NO - Nitric Oxide
O_2 - Oxygen

p - Of Carbon Phase

S - Sulfur

SO_2 - Sulfur Dioxide

T - Total

v - Sulfuric Acid

vs - Sulfuric Acid Saturation

1 - At Condition 1

2 - At Condition 2

Superscripts

A - Order of Reaction

m - Order of Reaction

n - Order of Reaction

p - Order of Reaction

q - Order of Reaction